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AND
WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua.... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo.
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

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[SEVENTH SERIES.]

JANUARY 1929.

I. *Thermal Diffusion of Rare Constituents in Gas-mixtures.*

By SYDNEY CHAPMAN, *F.R.S., Imperial College of Science and Technology, South Kensington, London* *.

I. *Thermal Diffusion and the Soret Phenomenon.*

§ 1. IT has been shown theoretically, by Enskog ⁽¹⁾ and the writer ⁽²⁾ independently, that a gradient of temperature existing in a gas-mixture produces a motion of relative diffusion of the constituents, additional to and independent of any motion of diffusion that may be in progress, owing to a gradient of concentration or other cause. If the temperature gradient be maintained constant in a closed vessel, a steady state will result, in which there is a concentration gradient along the same direction, of amount just sufficient to effect a balance between the rates of diffusion due to the gradients. This phenomenon has been experimentally verified by Dootson ⁽³⁾, Ibbs ⁽⁴⁾, and Elliott & Masson ⁽⁵⁾.

§ 2. A similar phenomenon in liquids was discovered experimentally by Ludwig ⁽⁶⁾ and Soret ⁽⁷⁾ long before the theoretical discovery of thermal diffusion in gases ; it is generally known as the Soret phenomenon or Soret effect. Many attempts to provide a theory of it have been made ⁽⁸⁾, but none seems to have been successful. This is scarcely surprising if, as seems likely, the Soret phenomenon at its simplest is the analogue for liquids of thermal diffusion in gases, and may in many cases be further complicated by dissociation-effects depending on temperature, and, in electrolytes, by electric effects. There may be some hope of arriving at a simple theory in those cases, if any exist, where these additional causes are paramount; but where pure thermal diffusion is the only or main cause (and it will be shown in the following pages that thermal diffusion in gases is capable of producing concentration gradients of the same order of magnitude as are found in the Soret effect in many liquid solutions), the prospect of arriving at an even approximately correct theory seems rather remote. This is not only because of the additional difficulties present in every branch of the kinetic theory of liquids, as compared with the corresponding theory for gases, but because the theory of thermal diffusion even in gases is unusually complex.

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* Communicated by the Author.

§ 3. In the case of gases, no success has yet attended any attempts to develop a simple physical theory of thermal diffusion that will indicate even the sign of the phenomenon, *i. e.* that will show which constituent tends to flow towards the warmer region; the theory has been obtained only by a complete mathematical treatment of the equations of detailed transfer in the gas-mixture. Arguments, such as were used by Meyer, that lead to simple theories of viscosity and thermal conduction, are not effective in the case of thermal diffusion, as I have recently shown (9); they are of too general a nature, and perhaps the reason why they are effective for viscosity and thermal conduction is because these phenomena likewise are general and unique in sign—friction always tending to retard relative motion, and heat to flow from hot regions to cold. But in thermal diffusion the constituent which tends towards the warmer region is generally, but not always, the lighter one, nor does the effect depend essentially on a difference of mass, since thermal diffusion can occur in mixtures of gases of equal molecular weight (10). The effect depends both on the masses and on the diameters or fields of force of the molecules, in a manner expressible, even to a first approximation, only by formulæ of much complexity. The formulæ for the Soret effect in liquids and its dependence on the detailed physical properties of the molecules will probably be still more complicated.

§ 4. Though it is depressing thus to dwell on the difficulties which appear to beset the theoretical treatment of the Soret phenomenon, a proper estimation of them may prevent waste of effort on unduly simple methods that are foredoomed to failure. It may be suggested that, where possible, any arguments on which it is proposed to base a theory of the Soret effect be first applied to the simpler case of thermal diffusion in gases, where an exact theory is available by which to test the results obtained. These remarks naturally do not apply to theories of the Soret effect in those cases, if any, where changes of dissociation, or electrical effects, can be shown to constitute the primary cause.

These considerations, applied to a recent attempt (11) by the writer to develop a theory of the Soret effect for Brownian grains suspended in a liquid at non-uniform temperature, led to the same unhopeful conclusion that the problem was too difficult for solution by the relatively elementary methods there used, though the work was not without valid and interesting results in relation to the distribution of the Brownian displacements in the case of non-uniform temperature.

II. *Thermal Diffusion of Rare Constituents in Gas-mixtures.*

§ 5. This work, however, turned my attention to the special case of thermal diffusion that bears most closely on the Soret effect as usually measured, namely, in solutions of small concentration. In this case the general formulæ for gas-mixtures become somewhat simplified, and it may be of interest to physicists and chemists to have them set out and illustrated by a few examples, particularly since the complete formulæ are repellent in their complexity.

The chief point of interest thus brought out is that thermal diffusion in gas-mixtures can produce a large proportionate change in the concentration of a rare constituent. Let the fractional concentration (by volume) of the two constituents be denoted by c_1, c_2, so that

$$c_1+c_2=1. \qquad \dots\dots \qquad (1)$$

Ordinary ratios of absolute temperatures (T) produce only small absolute changes in c_1 and c_2, whatever their values, and when neither c_1 nor c_2 is very small the change in either is a small proportion of the mean value, so that thermal diffusion seems to be a weak separating agent. But if c_1 (say) is very small, the difference between its values in the hot and cold regions of the containing vessel, though still small compared with unity, may be a large proportion of the mean value of c_1. This fact may be of importance in some chemical or physical experiments where a rare constituent has special properties. Were it not for the continual mixing by winds, it would probably have an important influence on the distribution of the small amount of ozone which is known to exist in the upper atmosphere.

§ 6. The equation determining the steady distribution of a gas-mixture in which the absolute temperature T is variable in the direction of x (say) is

$$\frac{\partial c_1}{\partial x} = -k_T \frac{\partial T}{T\partial x}. \quad \ldots\ldots \quad (2)$$

No separate equation for c_2 is needed, since $c_2 = 1 - c_1$. The first constituent will be taken to be the rare one, so that c_1 will later be assumed small. In (2), $k_T = D_T/D_{12}$, where D_T and D_{12} are respectively the coefficients of thermal and ordinary diffusion (2). It can be shown that k_T tends to zero with either c_1 or c_2, and that, writing

$$k_T = c_1 c_2 \alpha, \quad \ldots\ldots\ldots \quad (3)$$

in general α does not tend to zero with c_1 or c_2.

If c_1 is small, and c_2 therefore nearly equal to unity, (2) may be written in the approximate form

$$\frac{1}{c_1}\frac{\partial c_1}{\partial x} = -\frac{\alpha}{T}\frac{\partial T}{\partial x}. \quad (c_1 \text{ small}) . \quad (4)$$

In certain circumstances α may be treated as constant in this equation, and then there exists the simple solution

$$c_1 \propto T^{-\alpha}. \quad (c_1 \text{ small, } \alpha \text{ constant}) \quad (5)$$

In other cases α is approximately proportional to T^β, where β is a constant, and then (4) has the solution

$$\log_e c_1 = \text{constant} - \alpha/\beta, \quad (c_1 \text{ small, } \alpha \propto T^\beta) . \quad (5\,a)$$

where now T is involved, on the right, through α.

The gas-mixture is here supposed to be at rest in a steady state in a tube or other vessel of which the dimensions are large compared with the molecular mean free paths, so that the pressure is uniform; α then depends only on c_1, T and the properties of the molecules. If the absolute change of c_1 along the tube is small, its influence on α will be negligible. The total variation of T along the tube is supposed not small, but in some cases α is independent of T, when (5) is the correct solution, while in other cases α is proportional to

T^{β} (where β is generally less than $\frac{1}{2}$), when (5 *a*) is the correct solution.

If α is positive, the proportion of the rare constituent will decrease towards the warmer regions; if negative, it will increase towards these regions. Either sign is possible, according to the nature of the molecules of both kinds.

III. *General Formulæ for the First Approximation to α.*

§ 7. The complete general expression for α is obtained in the form of the quotient of one infinite determinant by another, and only in one or two special cases can this expression be reduced to a simple form. In general it is impracticable to do more than consider the first few approximations to the complete expression, and even the first approximation, which alone will be considered here, is a lengthy formula. Fortunately it is correct to within a few units per cent.

The first approximation, which may be denoted by $\alpha(1)$, for the general case of spherically symmetrical molecules of any kind, is as follows, where M_1 and M_2 denote the molecular *weights* of the constituents 1 and 2:

$$\alpha(1)=$$

$$\frac{\frac{5}{2}\left\{\frac{1}{c_1\sqrt{M_2}}(\alpha_{01}\alpha_{1-1}-\alpha_{0-1}a_{11})+\frac{1}{c_2\sqrt{M_1}}(\alpha_{0-1}\alpha_{1-1}-\alpha_{01}a_{-1-1})\right\}}{a_{11}a_{-1-1}-\alpha^2_{1-1}}, \quad \ldots \quad (6)$$

where

$$a_{11}=\alpha_{11}+(c_1\ c_2)\alpha_{11}', \quad \ldots\ldots \quad (7)$$

$$a_{-1-1}=\alpha_{-1-1}+(c_2/c_1)\alpha_{-1-1}, \quad \ldots\ldots \quad (8)$$

and the various factors α_{rs} are independent of c_1 and c_2, but are complicated functions of the temperature and of the masses and other properties of the molecules. They can be expressed as follows:—

$$\alpha_{01}=\mu_2{}^2M_1{}^{\frac{1}{2}}\left\{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)\right\}, \quad \ldots\ldots \quad (9)$$

$$\alpha_{0-1}=-\mu_1{}^2M_2{}^{\frac{1}{2}}\left\{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)\right\}=-\mu_{12}{}^{\frac{3}{2}}\alpha_{01}, \quad \ldots \quad (10)$$

$$\alpha_{11}'=\frac{1}{3}\Omega_1(2,\,2),\qquad \alpha_{-1-1}'=\frac{1}{3}\Omega_2(2,\,2),\quad .\ .\ .\ .\ .\quad (11)$$

$$\alpha_{11}=\mu_2\left\{\left(\frac{55}{4}\mu_1^2-\frac{25}{2}\mu_1+\frac{25}{4}\right)\Omega_{12}(1,\,1)-5\mu_2^2\Omega_{12}(1,\,2)\right.$$
$$\left.+\mu_2^2\Omega_{12}(1,\,3)+\frac{4}{3}\mu_1\mu_2\Omega_{12}(2,\,2)\right\},\ .\ .\ .\ .\quad (12)$$

$$\alpha_{1-1}=-(\mu_1\mu_2)^{\frac{3}{2}}\left\{\frac{55}{4}\Omega_{12}(1,\,1)-5\Omega_{12}(1,\,2)\right.$$
$$\left.+\Omega_{12}(1,\,3)-\frac{4}{3}\Omega_{12}(2,\,2)\right\}.\ .\ .\quad (13)$$

The expression for α_{-1-1} is obtainable from (12) by interchanging μ_1 and μ_2, which themselves are defined by

$$\left.\begin{aligned}\mu_1&=\frac{M_1}{M_1+M_2},\qquad \mu_2=\frac{M_2}{M_1+M_2},\\ \mu_{12}&=\mu_1/\mu_2=M_1/M_2,\qquad \mu_{21}=1/\mu_{12},\end{aligned}\right\}\ .\ .\quad (14)$$

so that

$$\mu_1+\mu_2=1.\ .\ .\ .\ .\ .\ .\ .\quad (15)$$

In the above expressions $\Omega_{12}(l,\,n)$ denotes a certain function of T depending also on M_1, M_2, and the law of force between the unlike molecules; $\Omega_1(l,\,n)$ denotes the same function of the law of force between like molecules of the kind 1, M_2 in Ω_{12} being replaced in Ω_1 by M_1; similarly for Ω_2.

By virtue of the relations (7), (8), (10) the equation (6) can be written in the form

$$\alpha(1)=\frac{5}{2}\mu_{12}M_1^{-\frac{1}{2}}\alpha_{01}\,\frac{c_1\{\mu_{12}\alpha_{11}'-\mu_{12}^{\frac{1}{2}}\alpha_{1-1}-\mu_{21}\alpha_{-1-1}\}-c_2\{\mu_{21}\alpha_{-1-1}'-\mu_{21}^{\frac{1}{2}}\alpha_{1-1}-\mu_{12}\alpha_{11}\}}{c_1^2\alpha_{11}'\alpha_{-1-1}+c_1c_2(\alpha_{11}\alpha_{-1-1}+\alpha_{11}'\alpha_{-1-1}'-\alpha_{1-1}^2)+c_2^2\alpha_{11}\alpha_{-1-1}'},$$
$$.\ .\ .\quad (16)$$

where the dependence of α (1) upon c_1 and c_2 is completely explicit.

§ 8. In the following we shall consider specially the case where the molecules of the first kind are rare, so that c_1 tends to zero and c_2 to 1. In this case (16) becomes

$$\underset{c_1\to 0}{\text{Limit}}\ \alpha(1)=\frac{5}{2}\mu_{12}M_1^{-\frac{1}{2}}\alpha_{01}(\mu_{12}\alpha_{11}+\mu_{21}^{\frac{1}{2}}\alpha_{1-1}$$
$$-\mu_{21}\alpha_{-1-1}')/\alpha_{11}\alpha_{-1-1}'.\ .\quad (17)$$

Owing to the disappearance of a_{11}' from (17), this being the only term in (16) that depends on the law of force between the molecules 1 (*cf.* (11)), it is clear that the value of $\alpha(1)$, or the effect of thermal diffusion on the concentration gradient of the gas-mixture, does not depend on the nature of the interaction between the rare molecules. This is natural, since when c_1 tends to zero their mutual encounters are infinitely less frequent than their collisions with the molecules 2.

Two special forms of this limiting value of $\alpha(1)$ may be noted here, in which the rare molecules 1 are either infinitely heavier or infinitely lighter than the numerous molecules 2, *i. e.* the cases

$$(a) \quad \mu_1 \rightarrow 1, \quad \mu_2 \rightarrow 0\,;$$
$$(b) \quad \mu_1 \rightarrow 0, \quad \mu_2 \rightarrow 1.$$

It is evident, on inspection of (9), (11), (12), (13), that in case (*a*) only the first term in the numerator of (17) remains in the limiting expression (17), whereas in case (*b*) only the third term remains. Thus, on proceeding to the limits, we have

$$\operatorname*{Limit}_{c_1\rightarrow 0,\ \mu_2\rightarrow 0} \alpha(1) = \frac{15}{2}\,\frac{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)}{\Omega_2(2,2)}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$\operatorname*{Limit}_{c_1\rightarrow 0,\ \mu_1\rightarrow 0} \alpha(1) = -\frac{5}{2}\,\frac{\Omega_{12}(1,2)-\frac{5}{2}\Omega_{12}(1,1)}{\frac{55}{4}\Omega_{12}(1,1)-5\Omega_{12}(1,2)+\Omega_{12}(1,3)}. \quad . \quad . \quad . \quad (19)$$

These results are independent of the order in which the two limits, for c_1 and μ_1, are approached.

§ 9. It may be noted that when the rare molecules are also the very light ones, the value of α is independent of the nature of the interaction between the numerous molecules 2 among themselves (*cf.* 19)). The latter move infinitely more slowly than the light molecules, owing to the approximate equality between the mean kinetic energies of peculiar motion of the molecules of the two kinds. Thus the heavy molecules are practically at rest, and the thermal diffusion depends only on the collisions of the rare, light, rapidly-moving molecules with the heavy stationary obstacles presented by the numerous molecules.

When, as in (18), the rare molecules are the heavy ones, thermal diffusion depends on the nature of the interaction both between the unlike molecules, and between the numerous light molecules among themselves.

It may also be remarked that case (*b*)—that of rare light molecules—is one of those in which the general theory of thermal diffusion can be replaced by a much simpler special theory, along lines first indicated by Lorentz $^{(12)}$ in connexion with the electron theory of metals. The exact expression for α (in place of the first approximation $\alpha(1)$ considered in (18)) can in this case be found. The general expression will not be given here, but in sections IV., V. the values for particular models will be quoted.

§ 10 The above formulæ can be further developed by inserting the appropriate values of the functions Ω. The general expressions for these functions will not be quoted here, but only the forms which they take for two specially simple types of molecular model, namely, rigid elastic spheres of diameters d_1, d_2, and point-centres of force varying as some constant (sth) power of the inverse mutual distance r, *i. e.* as r^{-s}; s will have suffixes 1, 12, or 2 according as the interaction refers to molecules 1 alone, 1 and 2, or 2 alone. The former model is, in a sense, a special case of the latter, corresponding to $s \to \infty$.

IV. *Rigid Elastic Spheres* *.

§ 11. In this case $\Omega(l, n)$ is independent of the first parameter l, being given, for all values of l, by

$$\Omega_{12}(l, n) = \tfrac{1}{16}(n+1)\,!\,(d_1+d_2)^2\{2\mathrm{RT}(\mathrm{M}_1+\mathrm{M}_2)/\mathrm{M}_1\mathrm{M}_2\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad (20')$$

where R denotes the gas-constant per gram-molecule, $8{\cdot}316 \, . \, 10^7$ ergs/°. Similarly

$$\Omega_2(l, n) = \tfrac{1}{2}(n+1)\,!\,d_2^2(\mathrm{RT}/\mathrm{M}_2)^{\frac{1}{2}}, \quad . \quad . \quad (21')$$

being obtained from (21') by changing the suffix 1 to 2 throughout; likewise for $\Omega_1(l, n)$.

Consequently

$$\Omega(l, n) = (n+1)\Omega(l, n-1), \quad . \quad . \quad . \quad (22')$$

whence it follows that

$$\mathrm{M}_1{}^{-\frac{1}{2}}\alpha_{01} = \tfrac{1}{2}\mu_2{}^2\Omega_{12}(1, 1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9')$$

$$\alpha_{11}{}' = \Omega_1(1, 1), \quad \alpha_{-1-1}{}' = \Omega_2(1, 1), \quad . \quad . \quad (11')$$

---

* The formulæ of this section are denoted by accented numbers (') to indicate that they refer to a special model, and are not general, like those in the preceding sections: the formulæ of section V. are denoted by (").

$$\alpha_{11}=\mu_2\left(\frac{13}{4}-\frac{5}{2}\mu_1+\frac{27}{4}\mu_1^2\right)\Omega_{11}(1,1), \quad . \quad (12')$$

$$\alpha_{1-1}=-\frac{27}{4}(\mu_1\mu_1)^{\frac{3}{2}}\Omega_{12}(1,1). \quad . \quad . \quad . \quad . \quad (13')$$

On substitution of these results into (17), this becomes

$$\underset{c_1\to 0}{\text{Limit}} \quad \alpha(1)=\frac{5}{4}\left\{(\tfrac{1}{2}\mu_1)^{\frac{1}{2}}(13-27\mu_1+44\mu_1^2)\left(\frac{d_1+d_2}{2d_2}\right)^2-4\mu_2\right\}$$
$$\div(13-10\mu_1+27\mu_1^2). \; (17')$$

On making μ_1 or μ_2 tend to zero, the following special cases of (18), (19) and the exact value of α in Lorentz's case are obtained:

$$\underset{c_1\to 0,\ \mu_2\to 0}{\text{Limit}} \quad \alpha(1)=\frac{5}{4\sqrt{2}}\left(\frac{d_1+d_2}{2d_2}\right)^2, \quad . \quad . \quad (18')$$

$$\underset{c_1\to 0,\ \mu_1\to 0}{\text{Limit}} \quad \alpha(1)=-\frac{5}{13}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19')$$

$$\underset{c_1\to 0,\ \mu_1\to 0}{\text{Limit}} \quad \alpha=-\frac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23')$$

V. *Molecules exerting Central Forces.*

§ 12. Suppose that the molecules are point-centres of force varying as r^{-s}, so that between unlike molecules 1, 2 the force is denoted by

$$K_{12}\frac{M_1M_2}{M_1+M_2}r^{-s_{12}}, \quad . \quad . \quad . \quad . \quad . \quad (24'')$$

and between two molecules 2, 2 by

$$\tfrac{1}{2}K_2M_2r^{-s_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25'')$$

The value of Ω in this case is given by

$$\Omega_{12}(l,n) = A(l,s_{12})\phi_{12}(s_{12})\Gamma\left(n+2-\frac{2}{s_{12}-1}\right), \quad (26'')$$

where

$$\phi_{12}(s_{12}) = \tfrac{1}{2}K_{12}^{\frac{2}{s_{12}-1}}\{2RT(M_1+M_2)/M_1M_2\}^{\frac{1}{2}\frac{s_{12}-5}{s_{12}-1}}, \quad (27'')$$

and $A(l,s_{12})$ is a pure number obtained as an integral which can only be evaluated by quadrature. Its values for $l=1, 2$ and various values of s are as follows, in terms of certain integrals $I_1(s)$, $I_2(s)$ that have been evaluated by various writers[(13)]:—

$$A(1, s) = \frac{1}{2\pi} I_1(s), \qquad A(2, s) = \frac{3}{2\pi} I_2(s), \quad . \quad (28'')$$

$s=$	2	3	5	7	9	11	15	21	25	∞
$I_1(s)=$	...	5·10	2·65	2·42	2·40	2·41	2·47	...	...	π
$I_2(s)=$	...	3·82	1·37	1·12	1·04	1·00	0·972	0·966	0·963	$\frac{1}{3}\pi$
$I_2(s)/I_1(s)=$	1	1·33	1·93	2·16	2·31	2·41	2·54	...	...	3

By substituting the suffix 2 for 1 throughout in (26″), $\Omega_2(l, n)$ is obtained, and similarly for $\Omega_1(l, n)$.

In the present case

$$\Omega(l, n) = \left(n+1-\frac{2}{s-1}\right)\Omega(l, n-1), \quad . \quad (22'')$$

where Ω and s have the same suffix 1, 12, or 2. Consequently

$$M_1^{-\frac{1}{2}}\alpha_{01} = \mu_2^2 \frac{s_{12}-5}{2(s_{12}-1)} \Omega_{12}(1, 1), \quad . \quad . \quad (9'')$$

$$\alpha_{11}' = \frac{1}{3}\left(3-\frac{2}{s_1-1}\right)\Omega_1(2, 1), \quad \alpha_{-1-1}' = \frac{1}{3}\left(3-\frac{2}{s_2-1}\right)\Omega_2(2, 1), \quad . \quad . \quad . \quad (11'')$$

$$\alpha_{11} = \mu_2\Bigg[\left\{\frac{55}{4}\mu_1^2 - \frac{25}{2}\mu_1 + \frac{25}{4} - 5\mu_2^2\left(3-\frac{2}{s_{12}-1}\right)\right. \\ \left. + \mu_2^2\left(3-\frac{2}{s_{12}-1}\right)\left(4-\frac{2}{s_{12}-1}\right)\right\} \\ + \frac{4}{3}\mu_1\mu_2\left(3-\frac{2}{s_{12}-1}\right)\{A(2, s_{12})/A(1, s_{12})\}\Bigg]\Omega_{12}(1, 1), \quad . \quad . \quad . \quad (12'')$$

$$\alpha_{1-1} = -(\mu_1\mu_2)^{\frac{3}{2}}\Bigg[\frac{55}{4} - 5\left(3-\frac{2}{s_{12}-1}\right) \\ + \left(3-\frac{2}{s_{12}-1}\right)\left(4-\frac{2}{s_{12}-1}\right) \\ - \frac{4}{3}\left(3-\frac{2}{s_{12}-1}\right)\{A(2, s_{12})/A(1, s_{12})\}\Bigg]\Omega_{12}(1, 1). \quad (13'')$$

The corresponding form of (17) is too complicated to be worth quoting here, but the following are the special forms of (18), (19) and the exact form of α in Lorentz's case:—

$$\underset{c_1\to 0,\ \mu_2\to 0}{\text{Limit}} \quad \alpha(1) = \frac{15}{4}\frac{s_{12}-5}{s_{12}-1}\frac{s_2-1}{3s_2-5}\frac{A(1, s_{12})}{A(2, s_2)}\frac{\phi_{12}(s_{12})}{\phi_2(s_2)}. \quad (18'')$$

$$\lim_{c_1\to 0,\,\mu_1\to 0} \alpha(1) = -\frac{s_{12}-5}{s_{12}-1}\,\frac{5(s_{12}-1)^2}{13(s_{12}-1)^2-16(s_{12}-1)+16}, \quad . \quad . \quad . \quad (19'')$$

$$\lim_{c_1\to 0,\,\mu_1\to 0} \alpha = -\frac{s_{12}-5}{2(s_{12}-1)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23'')$$

It may be noted that when $s_{12}=5$, α is always zero, whatever the other circumstances. This is the case, specially considered by Maxwell, of molecules which repel one another according to the inverse fifth power of the distance; for such molecules thermal diffusion does not occur. The result is true whatever the interaction between the molecules 1 alone, or 2 alone.

For other values of s_{12}, the sign of thermal diffusion is different (*ceteris paribus*) according as s_{12} is greater or less than 5.

Owing to the last factor in (18″), $\alpha(1)$ in this case is not independent of T, as in the cases (18′), (19′), (23′), (19″), (23″): in (18″) it appears from (27″) that

$$\alpha(1) \propto T^{\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29'')$$

where

$$\beta = \frac{1}{2}\left\{\frac{s_{12}-5}{s_{12}-1} - \frac{s_2-5}{s_2-1}\right\}; \quad . \quad . \quad . \quad (30'')$$

if, as for all ordinary gases, $s > 5$, β cannot exceed $\frac{1}{2}$.

§ 13. By comparison between (19″) and (23″) the ratio $\alpha(1)/\alpha$ for any value of s_{12} when $c_1 \to 0$, $\mu_1 \to 0$ can readily be found. The following table gives this ratio for various values of s_{12}, and also the ratio $\alpha(2)/\alpha$, where $\alpha(2)$ denotes the second approximation. These ratios refer exclusively to Lorentz's case, but give an idea of the degree of error involved in using $\alpha(1)$ in place of α: the error is greatest (for $s>5$) in the case $s=\infty$, corresponding to rigid elastic spherical molecules—*cf.* (19′), (23′).

$s_{12} =$	2	3	5	9	13	17	∞
$\alpha(1)/\alpha =$	0·77	1·11	1·00	0·89	0·85	0·83	0·78
$\alpha(2)/\alpha =$	1·01	1·01	1·00	0·95	0·93	0·92	0·88

It appears from this table that for $s>5$ the approximations $\alpha(1)$, $\alpha(2)$ are less than α; the first approximation is good, and the second still better. When the molecular masses are nearly equal, the error of the first approximation appears to be less than in Lorentz's case.

§ 14. The expression (18)″ can be put into a much simpler form in terms of (i.) the coefficient of diffusion D_{12} of the mixture, at any pressure p and at the temperature T, and (ii.) the coefficient of viscosity v_2 at temperature T, for the pure gas composed of the numerous, light constituent by itself—so long as we are content to use the first (fairly accurate) approximations $D_{12}(1)$, $v_2(1)$ to D_{12} and v_2. For by (22)″

$$\underset{c_1\to 0,\ \mu_2\to 0}{\mathrm{Limit}}\ \alpha(1)=\frac{15}{4}\frac{s_{12}-5}{s_{12}-1}\frac{\Omega_{12}(1,1)}{\Omega_2\,(2,2)}, \quad . \quad . \quad (31'')$$

while, quite generally,

$$\mathrm{D}_{12}(1)=\frac{3}{16\pi^{\frac{1}{2}}}\frac{\mathrm{M}_1+\mathrm{M}_2}{\mathrm{M}_1\mathrm{M}_2}\frac{\mathrm{R}^2\mathrm{T}^2}{p\mathrm{N}\Omega_{12}(1,1)}, \quad . \quad . \quad (32'')$$

$$v_2(1)=\frac{15}{16\pi^{\frac{1}{2}}}\frac{\mathrm{RT}}{\mathrm{N}\Omega_2(2,2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (33'')$$

where N denotes the number of molecules per gram molecule. Consequently (when $M_2/M_1\to 0$),

$$\underset{c_1\to 0,\ \mu_2\to 0}{\mathrm{Limit}}\ \alpha(1)=\frac{3}{4}\frac{s_{12}-5}{s_{12}-1}\frac{\mathrm{RT}}{p\mathrm{M}_2}\frac{v_2(1)}{\mathrm{D}_{12}(1)}; \quad . \quad . \quad (34'')$$

this expression is independent of the value of p at which D_{12} is measured, since $D_{12}\propto 1/p$.

From (33″), (26″), and (27″) it appears that

$$v_2\propto \mathrm{T}^{(s_2+3)/2(s_2-1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35'')$$

so that from a knowledge of the variation of v_2 with temperature, s_2 can be inferred. For helium its value is approximately 14.

§ 15. It is of interest to examine how nearly the limiting formula (18′) for $\alpha(1)$ agrees with the true value of $\alpha(1)$ when M_1/M_2 is large (or μ_2 small) but not infinite; and likewise for (19′), when M_1/M_2 (or μ_1) is small but not zero. This can readily be done by inserting illustrative values of μ_1 and μ_2 in (17′) and comparing them with the values (18′) or (19′).

When μ_2 is small, d_2 is likely to be not greater than d_1, and extreme values of the ratio of $\alpha(1)$ to the limiting value of $\alpha(1)$ given by (18′) can be found by taking $d_2=0$ and $d_2=d_1$. In this way, when $\mu_2=\frac{1}{30}$, $\mu_1=\frac{29}{30}$, or $M_1/M_2=29$ the actual value of $\alpha(1)$ is less than that given by (18)′ by from 3·5 to 4·2 per cent.; when $\mu_2=\frac{1}{50}$, $\mu_1=\frac{49}{50}$, or

$M_1/M_2=49$, the corresponding limits of error are 2·1 and 2·5 per cent. Thus when M_1 is 50 or more times as great as M_2, (18′) affords a close approximation to the actual value of $\alpha(1)$; (18′) is larger than the true value of $\alpha(1)$, but the latter is less than the true value of α, so that (18′) is likely to be nearly correct.

The error of (19′) when μ_1 is small but not zero is rather larger than in the corresponding case for (18′). Here the limits of error are found by taking $d_1=0$ and $d_1=d_2$. If $\mu_1=\frac{1}{50}$, $\mu_2=\frac{49}{50}$, or $M_2/M_1=49$, the actual value of $\alpha(1)$ is less than that given by (19′) by from 8 to 12 per cent., though (19′) is likely to be nearly equal to the true value of α if M_2/M_1 has this value.

The corresponding percentage errors of the formulæ (18″), (19″), (34″), for values of s between ∞ and 5, are likely to be less than for (18′), (19′).

VI. *Numerical Illustrations and Suggestions for Experiment.*

§ 16. The order of magnitude of the concentration gradient produced by thermal diffusion in a closed vessel can be illustrated most readily from the simple formula (23″), corresponding to the case where the rare constituent is very light. In this case α, besides being known exactly, depends only on s_{12}. The following are values of $-\alpha$ for various values of s_{12}; the case $s_{12}=\infty$ corresponds also to (23)′:—

s_{12}:	∞	25	21	17	15	13	11	9	8	7	6	5
$-\alpha$:	500	·417	·400	·375	·357	·333	·300	·250	·214	·167	·100	0

Since, by (5), $c_1 \propto T^{-\alpha}$, when α is constant, as here, the negative sign of α indicates that the proportion of the light rare constituent increases towards the hot region. The concentration-gradient produced may be illustrated by supposing the extreme absolute temperatures T, T′ (where T′>T) to be in the ratio $\frac{4}{3}$, as, for example, if T=300°, or 27° C., and T′=400°, or 127° C. The ratio of the corresponding values c_1, c_1' may be expressed as the percentage excess of c_1, *i. e.* by $100\left(\frac{c_1'}{c_1}-1\right)$, as in the following table:—

s_{12}:	∞	25	21	17	15	13	11	9	8	7	6	5
$100\left(\frac{c_1'}{c_1}-1\right)$ for $\frac{T'}{T}=\frac{4}{3}$:	15·4	12·7	12·2	11·4	10·9	10·1	9·0	7·5	6·4	4·9	2·9	0

§ 17. Much larger ratios of c_1 to c_1' for a given value of T′/T can be obtained, however, when the rare constituent is very heavy instead of very light. In this case (when $s > 5$) the rare constituent, being heavy, is more concentrated in the cold than the hot region, since α is positive.

The maximum effect is obtained in the case of molecules which behave like rigid elastic spheres. If M_1 much exceeds M_2, d_1 is likely to exceed d_2. The following table gives the values of $\alpha(1)$ for a gas-mixture composed of rigid spherical molecules, for various likely values of the ratio d_1/d_2, from 1 to 3 ; $\alpha(1)$ is found from (18′) to vary from ·88 to 3·54, implying considerable percentage changes of concentration (here reckoned as the percentage excess of c_1 over c_1') even when T′/T is only $\frac{4}{3}$, as the table shows.

d_1/d_2 :	1	$1\frac{1}{4}$	$1\frac{1}{2}$	$1\frac{3}{4}$	2	$2\frac{1}{4}$	$2\frac{1}{2}$	$2\frac{3}{4}$	3
$\alpha(1)$:	·884	1·12	1·38	1·66	1·99	2·32	2·97	3·10	3·54
$100\left(\frac{c_1}{c_1'}-1\right)$ for $\frac{T'}{T}=\frac{4}{3}$:	29	38	49	61	77	95	135	144	177

If $M_1/M_2 > 30$, these values of $\alpha(1)$ are unlikely to be less than the true values of α (*cf.* § 15), so that the large percentage changes of concentration are not over-estimated, for rigid spherical molecules.

§ 18. Most molecules, however, are "softer" than these, and correspond more nearly to molecules of the type considered in section V. for some finite value of s. The percentage excess of c_1 over c_1' for such molecules will be less than for the case $s=\infty$, and vanishes altogether for $s=5$. Moreover, unless $s_{12}=s_2$ so that $\beta=0$ (*cf.* (30″)), the law connecting the concentration c_1 with the temperature will not be $\log(c_1/c_1') = \alpha \log(T'/T)$, but that given by (5 *a*).

In this case, since $\alpha \propto T^\beta$,

$$\log_e \frac{c_1}{c_1'} = \frac{\alpha' - \alpha}{\beta} = \frac{\alpha}{\beta}\left\{\left(\frac{T'}{T}\right)^\beta - 1\right\}. \quad . \quad . \quad (36'')$$

If the viscosity v_2 of the light constituent (in the pure state) has been determined over a range of temperature, so that s_2 is known (*cf.* § 14), and if D_{12} is known at the temperature T and any pressure p, then α is a known multiple of $(s_{12}-5)/(s_{12}-1)$, and β is also known in terms of this quantity and s_2. Hence a measurement of c_1/c_1' suffices to determine s_{12}*, after which K_{12} can be determined from D_{12}.

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* The actual solution is probably best made by calculating the right-hand side of (36″) for two or three values of s_{12}, and interpolating.

This seems to afford the simplest method of finding K_{12} and s_{12} when the heavy constituent is obtainable only in small quantities.

It may be noted that β will be positive or negative, according as s_{12} is $>$ or $< s_2$ (both being supposed not less than 5); the greatest value numerically is $\frac{1}{2}$, when one s is ∞ and the other 5, *i. e.* when in one set of inter-actions the numerous molecules behave like rigid spheres, and in the other like Maxwellian molecules, so that different forms of Ω must be used in the numerator and denominator of (18)—one from Section V., the other from Section VI.

In general $\{(T'/T)^{\beta}-1\}/\beta$ differs little from $\log_e(T'/T)$ when T'/T is not too great: for example, if $T'/T=\frac{4}{3}$, $\log_e(T'/T)$ is ·218, while $\{(T'/T)^{\beta}-1\}/\beta$ is ·268 if $\beta=-\frac{1}{2}$, and ·310 if $\beta=\frac{1}{2}$. In such cases a first approximation to α can be derived by using the simple formula $\log(c_1/c_1')=\alpha\log(T'/T)$, appropriate when α is constant; this will give a first approximation to s_{12}, and consequently to β, by (30″). Then a close second approximation to α can be made by using this value of β in (36″).

§ 19. Perhaps the most interesting and important application of these results is the determination of the law of force between helium molecules and those of radium emanation. The forces between molecules of the inert gases are of special interest because of their relation to the equilibrium of crystals in which the atoms are ionized—a subject studied by Born (14) and, very extensively, by Lennard-Jones (15). Moreover, the radioactive property of the radium emanation enables its amount in a gas to be determinable with considerable accuracy, even when it is small. The mass-ratio of RaEm to He is 55·5, amply sufficient to justify the application of (18′) or (18″)—or (34″)—to a mixture in which the emanation is present to the extent of 2 or 3 per cent. at most. For helium c_2 and s_2 are known with ample accuracy, and in order to determine K_{12} and s_{12} it only requires a knowledge of D_{12} and $\log(c_1/c_1')$. The value of c_1/c_1' for $T'/T=\frac{4}{3}$ is not likely to be less than 1·2, corresponding to an excess concentration of RaEm by at least 20 per cent. in the cold region; the excess may well be much more, and can be increased by increasing the temperature ratio T'/T. Owing to the low concentration of the emanation, the time required for the steady concentration-gradient corresponding to the steady state of non-uniform temperature will be quite small.

It would also be of interest to determine in like manner the law of force between RaEm and the other inert gases Ne, A, Kr, Xe, though in these cases, since the mass-ratio is neither very large nor very small, the general formula (17) for α (1) must be used in working out the results, instead of the simpler special cases (18), (19). In all cases the RaEm may be a sufficiently rare constituent for (17) to be applicable, and no knowledge of the law of interaction between the RaEm molecules themselves is required. Another interesting gas-mixture, in which M_1/M_2 is large, so that (18) and its special forms (18′), (18″), (34″) can be used, is that of RaEm and hydrogen. Possibly other experiments might be made in which the heavy gas was mercury vapour, iodine vapour, or bromine vapour.

When accurate data of the kind suggested become available, it may be worth while to go to greater detail in the theory of thermal diffusion, considering further approximations to α, and taking account of the attractive force which most molecules appear to exert at greater distances.

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(9) Chapman, Phil. Mag. v. p. 630 (1928).
(10) Chapman, Phil. Mag. xxxiv. p. 146 (1917).
(11) Chapman, Roy. Soc. Proc. A, cxix. pp. 34 & 55 (1928).
(12) Lorentz, 'Theory of Electrons,' Note 29; also Jeans, 'Dynamical Theory of Gases,' 4th edition, Ch. viii., §§ 288-295.
(13) Chapman, Mem. Manchester Lit. & Phil. Soc. lxvi. p. 1 (1922); also Lennard-Jones, Roy. Soc. Proc. A, cvi. p. 441 (1924).
(14) Born, 'Atomtheorie des festen Zustandes.'
(15) Lennard-Jones (and collaborators), Roy. Soc. Proc. A, cix. p. 584 (1925), cxii. p. 230 (1926), and numerous earlier papers there cited.

II. *On Groups of Electrons in the Geissler Discharge.* By K. G. Emeléus, *M.A., Ph.D., Lecturer in Physics, and* W. L. Brown, *M.Sc., Demonstrator in Physics, The Queen's University of Belfast* *.

1. *Introduction.*

IN two previous communications †, accounts have been given of some results obtained by employing cold exploring electrodes to analyse glow discharges from cold cathodes, the methods used being those which have been developed by Langmuir and Mott-Smith ‡. The object of these investigations was to find the distribution of potential through a discharge which had no positive column, and to correlate the magnitudes of the electric fields in it with the concentrations and temperatures of the slow conducting electrons. In both, evidence was obtained that a group of fast electrons was present in the negative glow, including some with an energy of the order of 80 electron volts, but no detailed study of these was then made, since it was realized that more data would be required before even their existence could be regarded as definitely established. This uncertainty arises from the fact that fast electrons can only be detected when there is a sheath of positive ions round the collecting electrode, and that serious departures from the laws which should govern the reception of the latter have been recorded, although the discrepancies observed have now been at least partially removed §. The usual difficulties are, moreover, exaggerated in the present case by other unfavourable circumstances, the chief of which are:—

(*a*) The concentrations of ions and electrons are small, which makes it necessary to use relatively large collectors, upon which thick ionic sheaths form.

(*b*) Gas has to be used at a pressure of about 1 mm. Hg, so that the motion of a positive ion in traversing a thick sheath is not free, whilst the number of collisions that it makes is nevertheless not large.

(*c*) Conditions vary rapidly with position in the discharge, so that a collector is usually receiving ions and electrons from a region through which their concentrations are not constant.

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* Communicated by the Authors.

† Emeléus, Proc. Camb. Phil. Soc. xxiii. p. 531 (1927). Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

‡ Langmuir & Mott-Smith, Gen. El. Rev. 1924.

§ Penning, *Konink. Akad. Wet. Amsterdam*, xxxi. p. 1 (1927). Morse & Uyterhoeven, Phys. Rev. xxxi. p. 827 (1928).

For these reasons we have now made a more extended series of measurements, from which we have concluded that fast electrons, which will be referred to, initially without implication as to their origin, as *primary* electrons, are really present, and we have obtained, incidentally, some information about the slower *secondary* and *ultimate* groups which confirms and extends results already published.

2. *Experimental Arrangements.*

The present arrangements have already been described *. Both thermionic diodes and wire resistances have been used to regulate the main discharge, currents of up to 5 milliamps. being passed at potentials between 250 volts and 400 volts. A switch was inserted so that the collector could be connected either to anode or cathode. In analysing the experimental data, we have worked with the ratio of the current to the collector to the current to the main cathode, to compensate approximately for fluctuations in the main discharge. The gases used were neon (containing 2 per cent. of helium), argon, hydrogen, and, for a few runs, oxygen. The argon was purified by arcing in the experimental tubes, or by passing a heavy glow discharge between magnesium electrodes in an auxiliary tube; hydrogen was admitted through a palladium regulator, whilst the oxygen was taken from a commercial cylinder. The discharge-tubes were cylinders, 3–4 cm. in diameter, and bulbs of various sizes. No attempt was made to obtain high purity of the gases, since it was felt that not enough was known of the general nature of the phenomena to warrant the elaborate precautions required to do this. The results were not affected, however, when mercury and carbon vapours were allowed access to the tubes by removal of liquid air from the traps. Glass-metal seals have been employed in most instances, and when this was impracticable, well-fitting dry joints made vacuum-tight with an external rim of picein. The collectors were usually bombarded with positive ions at 450 volts before taking a run, but omission to do this was again without effect. The pressure of the gas was recorded directly by a McLeod gauge, without any attempt being made to allow for local changes in temperature in the discharge-tube.

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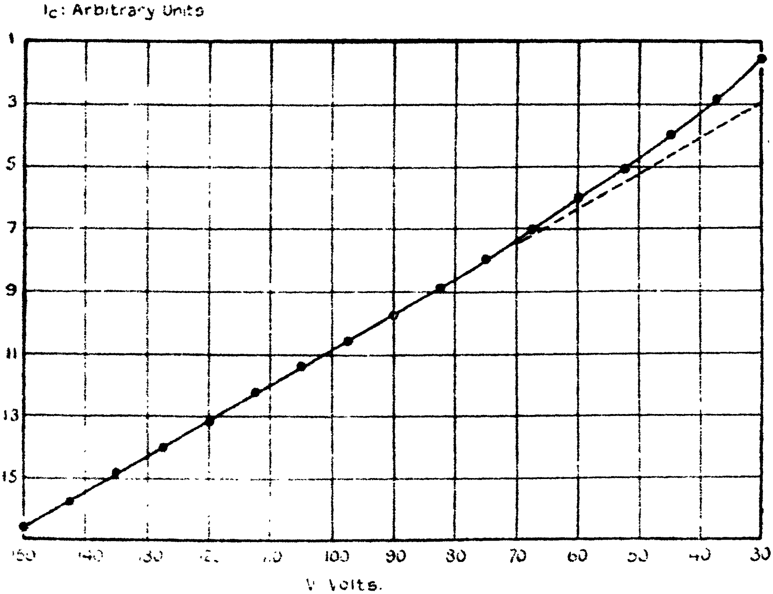
* Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

The first runs showed that the number of primary electrons was small, and that their distribution of velocities was approximately Maxwellian. Since the electron current to a collector at a given retarding potential is determined by its area, and the corresponding positive ion current by the outer area of the positive ion sheath, large collectors of small curvature were therefore used subsequently, with the object of keeping the ratio of the area of the sheath to the area of the collector as small and as nearly constant as possible.

Fig. 1.



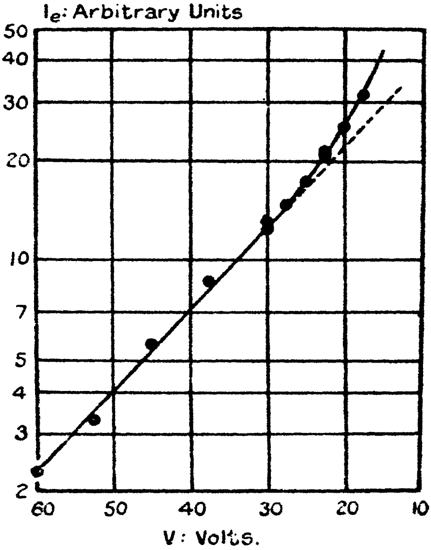
Net positive ion current to collector (I_c) for various potentials of collector negative to the anode (V): run 113.

3. *The Primary Group.*

Part of a collector characteristic, which is typical of some 150 which have been obtained in the present investigation from runs in the negative glow and Faraday dark space, is shown in fig. 1. The tube used was that described in § 4, the collector being in the middle of the negative glow, with its centre 0·25 cm. from the cathode, which was 0·90 cm. from the anode. The tube contained neon at a pressure of 1·37 mm. Hg, and was passing a current of 1·65 milliamps.

at 338 volts. For high accelerating potentials for positive ions the characteristic is practically linear, the current increasing with potential both because of the increase in the outer area of the sheath, and from causes referred to in § 1, but when about 70 volts negative to the anode, it takes a distinct additional upward trend. On extrapolating the almost straight part to lower collecting voltages, and analysing the difference between the experimental line and the extrapolated line by plotting current against voltage on semi-logarithmic paper in the usual way, three groups of

Fig. 2.



Semi-logarithmic plot of primary electron current (I_e) against collector potential negative to the anode (V).

electrons were found to be present. The line for the primary electrons is shown in fig. 2. The space potential was 10 volts negative to the anode. The difference between the two lines is at first small, and the primary temperature evidently cannot be found with great accuracy, so to obtain an idea of the reproducibility of the numbers, this run was made with the potential of the collector brought from a high negative potential through the space potential, and a second was then taken with the conditions otherwise unaltered, but the potential changes made in the reverse direction. The temperatures recorded were 26·4, 3·9, 0·94 volts, and 26·4, 3·4, 0·96 volts respectively; the identity of the primary temperatures is fortuitous, and the error in their determination is not less than ±3 volts. Two other examples of similar curves—in which all the experimental points are not shown—occur in fig 7.

Similar curves were obtained in the Faraday dark space in neon, argon, and hydrogen at various pressures, with a tube in which the cathode was a disk of nickel 0·85 cm. in diameter, backed with mica and supported by a glass-sheathed stem at the centre of a bulb 11 cm. in diameter; the anode was a piece of stout nickel wire situated close to the wall, and the collector a small cylinder of copper 1 mm. in diameter and 2 mm. long. The lead to the collector was separate from the pinch holding the leads for the anode and cathode. This showed that the appearance attributed to the primary group was not due to any action of the walls of the tube, nor to construction of the main discharge by the positive ion sheaths on the collector, which were often 3–4 mm. in diameter, and also made it improbable that it was due to collection from an inhomogeneous discharge, since conditions are more nearly uniform in the Faraday dark space than in the negative glow.

Runs in which the collector was a flat disk with a guard-ring gave characteristics of the same type, both when the guard-ring was held at the same potential as the disk and when it was floating, showing that the effect was not due to interaction between the positive ion sheaths on the collector and on neighbouring surfaces; the temperatures were the same in the two cases within the limits of experimental error. The primary group also appeared both when the collector was touching its insulating support in a part exposed to the discharge, and when it was protected from the discharge without actual contact.

The variety of conditions under which the primary group appears makes it very improbable that the effect is in any way due to the collector beginning to function as a main anode for the tube, especially since there is no marked change in the main current until the space-potential is passed and electrons begin to be collected in an accelerating field.

It was considered possible that the upward break in the characteristic might be due to a change in the type of motion of the positive ions, from an almost free fall through the thin sheaths present at small collecting voltages, to a species of mobility motion through the thicker sheaths present at higher collecting voltages. We have been unable to disprove this by direct experiment, but we consider that the relatively sudden first appearance of the primary group is distinct from the likely changes in curvature of positive ion characteristics intermediate between some that we have computed on the one hand from Langmuir and Blodgett's tables for the free fall of ions*, and on the other from McCurdy's for collision motion †. The form of these computed curves does, however, show strongly the uncertainty of extrapolating to lower collecting voltages the positive ion line for higher collecting voltages.

During the course of this and the previous investigations, numerous tests were made to find if oscillations were occurring in the discharge system. Usually they were absent, but occasionally some of small amplitude, probably similar to those described by Appleton and West ‡, were detected. They were without effect upon the primary group. We have not examined the system by means of Lecher wires, but it is extremely unlikely that large amplitude oscillations of very high frequencies occurred with the small currents that were passed through our tubes §.

There is no systematic departure of the relation between log *i* and V for the primary group from the linear one required by a Maxwellian distribution of velocities, although some of the curves plotted on semi-logarithmic paper were definitely concave to the axis of voltage. However, no difference was found in this respect between the semi-log plots for a disk collector shielded from the cathode dark space and exposed to it, respectively, even although the collector was, from the appearance of the sheaths upon it, certainly drawing upon the ions in the cathode dark space in the latter case. The relation was likewise nearly linear for a collector consisting of a hemispherical piece of nickel, 2 mm. in diameter, placed with its axis perpendicular to the axis of the main discharge at the centre of curvature of a small hollow cathode, which would have been expected to concentrate any directed particles. It has nevertheless to be emphasized that large departures from a linear relation might pass unnoticed for the higher retarding voltages for electrons, because of the small differences between the experimental and the extrapolated lines, and also that a considerable drift velocity may be superposed upon a random motion without marked distortion of the linear semi-log plot*.

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* Langmuir & Blodgett, Phys. Rev. xxii. p. 347 (1923).

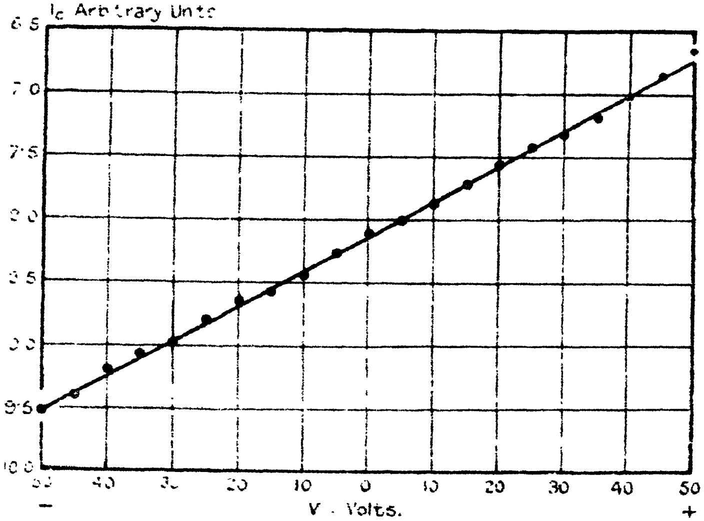
† McCurdy, Phys. Rev. xxvii. p. 157 (1926).

‡ Appleton & West, Phil. Mag. xlv. p. 879 (1923).

§ *Cf.* Langmuir, Proc. Nat. Acad. Sci. xiv. p. 627 (1928).

With some of the tubes used it has been possible to follow the positive ion line (*cf.* fig. 1) through the potential of the cathode without it showing any change. An example of this is shown in fig. 3. The collector was the hemispherical one previously mentioned, and was situated in the middle of the negative glow of a 295 volt discharge through hydrogen at a pressure of 0·59 mm. Hg: the positive ion sheath preserved its normal appearance. In other cases the positive ion sheath developed bright inner and outer edges, whilst the current to the collector increased more rapidly with increasing potential than at lower voltages. Fig. 4, which shows this, was obtained with neon in the bulb tube described earlier in this section, the gas-pressure being 2 03 mm. Hg and the tube voltage 238; the collector was in the Faraday dark space. The collector was then evidently acting as cathode for an auxiliary discharge, with the bright parts representing the cathode glow and the negative glow. If a small collector was used under these circumstances, it was liable to become

Fig. 3.



Net positive ion current to collector (I_c) for various potentials of the collector relative to the cathode (V): run 26, collector acting normally.

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* Langmuir, Phys. Rev. xxvi. p. 585 (1925).

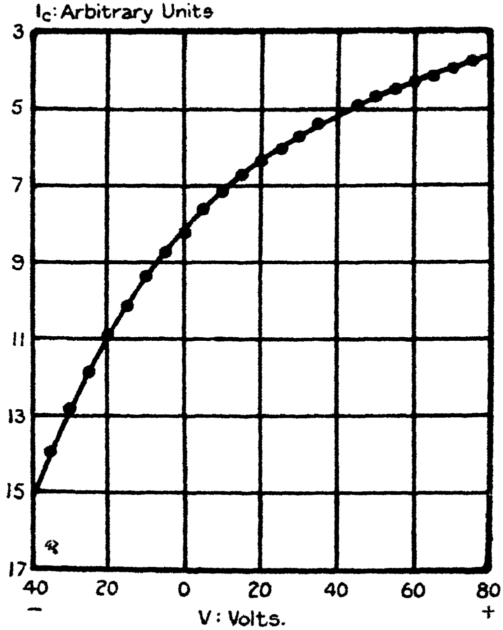
incandescent under the positive ion bombardment, particularly in argon, and an arc would strike to it.

It is concluded, from this evidence :—

(*a*) That the primary group of electrons is actually present in the discharge, and that the effects attributed to it are not inherent in the method of analysis.

(*b*) That the group has an approximately random distribution of velocities.

Fig. 4.



Net positive ion current to collector (I_c) for various potentials of collector relative to the cathode (V): run 13, collector acting as auxiliary cathode for main discharge.

(*c*) That it includes the majority of the fast electrons present, except very close to the cathode dark space (§ 4).

4. *Details of the Primary Group.*

The primary group was always present in the negative glow, where its average energy was usually between 20 and 45 electron-volts, irrespective of the gas used or of the applied potential. In the Faraday dark space it was absent at the higher pressures, *e.g.* at a pressure of 1·5 mm. Hg in argon; when present there, its energy was somewhat increased by an increase in the cathode fall in potential. Some results obtained with a tube 3 cm. in diameter, similar to that used in an earlier investigation, with both anode and cathode movable separately and fitting closely to the walls, are contained in Table I. The collector was an iron sphere, 0·32 cm. in diameter, situated on the axis of the tube. The fall of potential at the anode (run 107) is close to the ionization potential of neon (21·5 volts), as has been found by Penning *, when, as in this case, there was an anode glow present. The concentration of the primary group falls off on receding from the cathode far more rapidly than the concentrations of the slower groups.

TABLE I.

Run.	Collector to cathode, cm.	Space potential, volts negative to anode.	Temperatures, volts.			Concentrations, 10^7.			Position.
			I.	II.	III.	I.	II.	III.	
105 ...	0·48	21·5	19·2	4·0	0·5	3·7	38	332	Negative glow.
106 ...	0·62	20·0	34·5	3·9	1·2	2·5	36	142	
107 ..	0·90	20·0	32·2	11	1·9	0·3	22	121	Faraday dark space.

Tube described in § 4:—Gas-neon, pressure – 1·36 mm. Hg; anode cathode, 1·06 cm.; current 3·3 milliamps.; applied potential, 385 volts; anode glow present.

Other results obtained with the same system of electrodes are collected in fig. 5, *a–f*, and fig. 6, *g–l*. Both refer to discharges through argon, the pressures being 1·10 mm. Hg (*a–c*, *g–i*) and 0·41 mm. Hg (*d–f*, *j–l*), the applied potentials 370 and 374 volts, and the tube currents 0·75 milliamp. and 0·79 milliamp. respectively. In the former case the cathode dark space was about 0·35 cm. thick, and in the latter about 0·5 cm. The main electrodes were 2·85 cm. apart in each case, and there was no anode glow. In the figures the numerals I., II., and III. refer to the primary, secondary, and ultimate electrons respectively, and the distances are measured from the cathode; the centre of the negative glow occurred at about the maximum of concentration for the ultimate electrons. The gas was sufficiently pure to show a primary dark space *. At the higher pressure there was a direct anode fall in potential of 7 volts, and at the lower pressure a reversed anode fall in potential of 10 volts. Local changes are, of course, inevitably smoothed over by the use of a large collector, but bearing this in mind, the curves for the secondary and ultimate groups are concordant with those obtained by Emeléus and Harris. In particular, the ultimate

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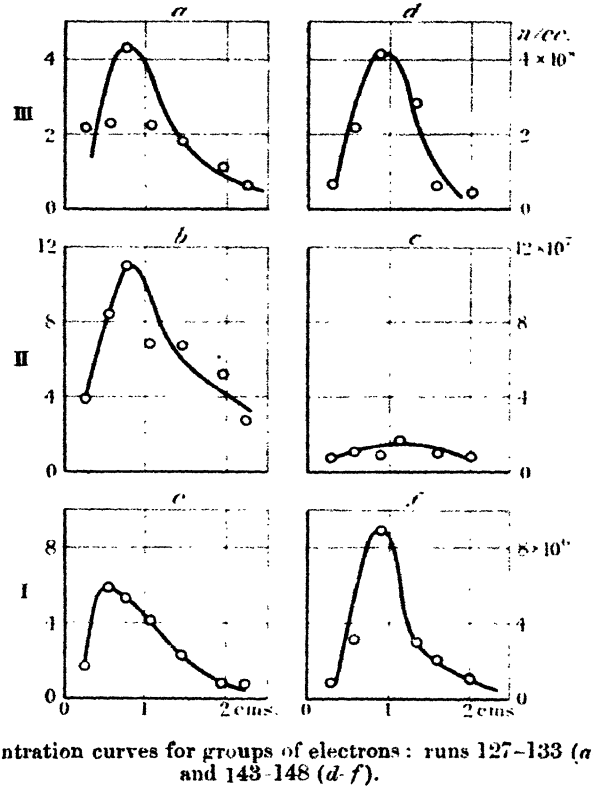
* Penning, *Physica*, v. p. 217 (1925).

Fig. 5.



Concentration curves for groups of electrons: runs 127–133 (*a–c*) and 143–148 (*d–f*).

electrons carry most of the random current, and the secondary electrons, which were not detected at the lower pressure before, are here only present in small numbers at 0·41 mm. Hg. In corresponding parts of the discharge the electron temperatures are higher at the lower pressures.

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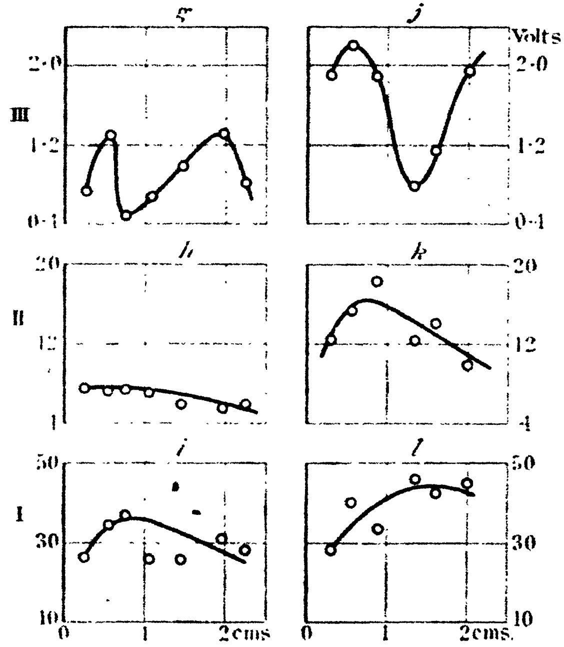
* Aston & Watson, Proc. Roy. Soc. A, lxxxvi. p. 168 (1912).

The points on the curves of concentration and temperature for the primary electrons (*c*, *f*, *i*, *l*), in drawing which account has been taken of the results of other series of runs, although somewhat scattered, exhibit certain regular features. The temperatures are again higher at the lower pressure, and, as has also been found in numerous other runs, both temperatures and concentrations have a maximum at about the brightest part of the negative glow at the higher pressure, and the concentration, if not also the temperature, a maximum there at the lower pressure. These observations are intimately connected with another point noticed in the present work, and in that of Emeléus and Harris*, which is illustrated by fig. 7, in which parts of a pair of collector characteristics used in connexion with figs. 5 and 6 are reproduced. The space potentials are shown by vertical lines on the produced positive ion lines. To the negative side

Fig. 6.



Temperature curves for groups of electrons: runs 127–133 (*g*–*i*) and 143–148 (*j*–*l*).

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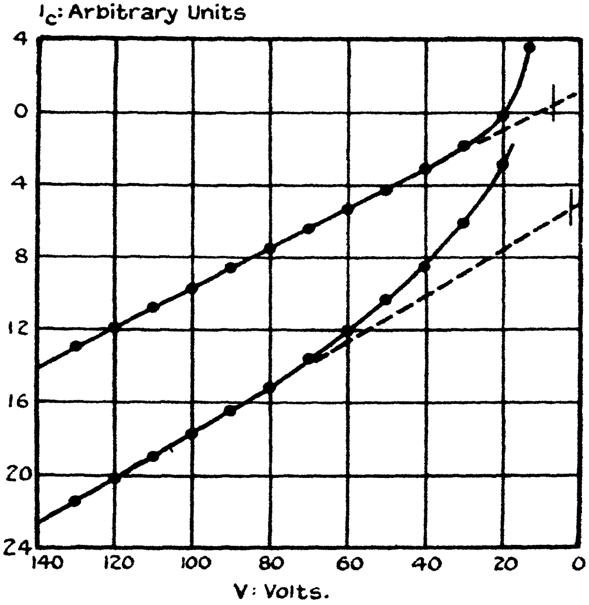
* Emeléus & Harris, Phil. Mag. iv. p. 49 (1927).

of the negative glow—upper curve—the latter extrapolates to an electron current at the space-potential; in parts of the discharge more remote from the cathode—lower curve—the line extrapolates to a positive ion current at the space-potential. The uncertainty involved in the extrapolation is probably such that the positive ion line should actually cross the voltage axis on the negative side of the space-potential more frequently than we have assumed. Near to the cathode there are apparently faster electrons than those in the primary group included with the positive ions, although it has hitherto been impossible to resolve them. The only work we have been able to trace in which it has been shown directly that fast electrons occur in the cathode dark space or negative glow for a cathode fall in potential of a few hundred volts is that of Dauvillier *, who detected photo-electrically the L-radiation of argon, which requires for its

Fig. 7.



Net positive currents to collector (I_c) for various potentials of the collector negative to the anode (V) under different conditions: runs 133 (above) and 132 (below).

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* Dauvillier, *Journ. d. Physique*, vii. p. 369 (1926).

excitation not less than 240 volts, from near the positive boundary of the cathode dark space under similar conditions. The evidence usually adduced in support of their presence from spectro-photometric studies of the negative glow does not take sufficient account of the complicated process that may give rise to the emission of light there.

5. *Discussion of Results.*

The data obtained so far are inadequate to serve as a basis for a complete test of the theory of the negative glow and Faraday dark space given by Morse[*], and are being extended, but certain points may be considered at this stage. It appears probable from the results of § 4 that the primary group is initially formed in the negative side of the negative glow from a faster and probably directed stream of electrons entering it from the cathode dark space, and that the existence of a maximum of ionization and luminosity in the middle of the negative glow is connected with the full development of the primary group. The average energy of the primary electrons in this part of the discharge is also about what would be expected on this view of their origin from Langmuir and Jones's measurements of the mean free paths of electrons[†], taken in conjunction with K. T. Compton and Morse's theoretical analysis of the normal cathode dark space[‡]. The approximately Maxwellian distribution of velocities found in the primary group is understandable in view of the small electric field in the negative glow, and the still unexplained fact that groups of electrons acquire a random motion in a region of intense ionization more readily than can be explained on the usual kinetic grounds[§].

The persistence of the primary group in the Faraday dark space is less readily accounted for, since it has long been recognized that even faster electrons than those now under consideration cannot penetrate far into it. Their distribution of velocities indicates, however, that they are in some sort of equilibrium, in which those which disappear by collision and by diffusion to the walls are partly regenerated by another agent, whilst the value of their average energy, which is usually somewhat above that required for ionization of the gas-molecules, suggests that some effect of the neutralization of positive ions may come into play. A mechanism which might produce new primary electrons is the converse of ionization by collision, with a system of two slow electrons and one positive ion passing into one consisting of a neutral, probably excited molecule, and a single fast electron. Lines of O III. and Ne III. occur in the spectrum of the negative glow of a discharge at 440 volts *, so that the recombination would include the partial neutralization of multiply-charged ions, with production of faster electrons than in the neutralization of singly-charged ions. Paschen has found continuous spectra beyond the series limits in the spectrum of the light from the negative glow in helium †, showing that the corresponding two-body interaction of a single slow electron and a positive ion, which results in the production of a neutral atom and radiation takes place, although it is not clear how this observation can be reconciled with the three-body theory of the recombination of ions proposed by J. J. Thomson ‡. Primary electrons might be formed in a positive column in this way, but although some curves which we have obtained in neon could be taken to indicate that they are present, further investigation of this part of the discharge is desirable. If this explanation of the persistence of the primary group in the Faraday dark space is correct, it would be expected to have a less energy, probably of the order of 12 volts, in discharges through mercury vapour, with an ionization potential of 10·4 volts.

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[*] Morse, Phys. Rev. xxxi. p. 1003 (1928).

[†] Langmuir & Jones, Phys. Rev. xxxi. p. 357 (1928).

[‡] K. T. Compton & Morse, Phys. Rev. xxx. p. 305 (1927).

[§] Langmuir, *Zeits f. Physik*, xlvi. p. 271 (1928).

It is very puzzling why two groups of slow electrons should be present in this and other discharges, although there is now no question of their separate existence §. There is no evidence as to how far these secondary and ultimate groups are produced directly from the primary group by collisions with gas-molecules, and how far they are produced by processes involving cumulative ionization and ionization by metastable atoms and by radiation. In gases in which there is a Ramsauer minimum of the free paths of electrons, this will tend to maintain the slow electrons in two groups, of greater and less energy than corresponds to the minimum, which does, in fact, often occur at about the average energy of the secondary and ultimate groups.

6. *Summary.*

Measurements of collector characteristics have been made in the Geissler discharge from a cold cathode in argon, neon, hydrogen, and oxygen, at pressures of about 0·1 cm. Hg, for conditions not far from those at normal cathode fall of potential, from which it is concluded that there is present in the negative glow, and at the low pressures, in the Faraday dark space, a group of fast electrons with a distribution of velocities that is approximately Maxwellian, and an average energy of the order of 25 electron-volts. It is suggested that they are produced initially by electrons passing into the negative glow from the cathode dark space, and that they are maintained by a process which is the reverse of ionization by collision. A possible effect of the Ramsauer minimum of the free paths of electrons is pointed out, in the persistence of two groups of slow electrons in the discharge.

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* F. M. Chambers & N. M. Carmichael (unpublished work).

† Paschen, *Sitz. Preuss. Akad. Wiss.* xvi. p. 135 (1926).

‡ J. J. Thomson, Phil. Mag. xlvii. p. 337 (1924).

§ v. Voorhis, Phys. Rev. xxx. p. 318 (1927).

We are indebted to Prof. E. V. Appleton, F.R.S., for a gift of copper-clad wire and valve pinches which has materially reduced the labour of building the numerous tubes required.

III. *Three-Dimensional Motion of an Electron in the Field of a Non-Neutral Atom.* *By* M. A. Higab, *M.Sc., Ph.D., Lecturer in Applied Mathematics in the Egyptian University, Cairo* *.

IN the Phil. Mag. xx. pp. 244–245 (1910) an attempt to deal with the three-dimensional motion of a particle under the effect of a doublet was made by Sir J. J. Thomson. In this paper, although the equations of motion were integrable, yet Sir J. J. Thomson considered only steady motion. The problem was resumed by Sir J. H. Jeans in the Phil. Mag. xx. pp. 380–382 (1910), who integrated the equations of motion and obtained certain results of interest. Physicists are generally convinced that the structure of a neutral atom of an element follows the lines associated with the names of Rutherford and Bohr. In such an atom the total charge is zero, and it behaves towards an electron sufficiently far away like a doublet.

Suppose that by some means or other this neutral atom loses or gains a charge. In this case the atom behaves like an electric doublet plus or minus an electric charge.

The problem is thus "To find the motion of an electron

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* Communicated by Prof. A. M. Mosharrafa.

(supposed to be negatively charged) under the effect of an electric doublet, acted upon at the same time by a central force inversely proportional to the square of the distance from the doublet itself."

We shall assume that the electron carries unit charge per unit mass, and that the electric charge is placed at the centre of the doublet; also that the axis of the doublet is fixed.

The problem is, as a matter of fact, suggested by Sir G. Greenhill (Phil. Mag. xlvi. pp. 372, 376, 1923), who, however, restricts the discussion to two dimensions. He shows that the problem can be dealt with in connexion with Euler's method for the path of a particle in the field of two fixed spheres. Sir G. Greenhill suggests the discussion of possible closed figures; and it is the object of the present paper to investigate the possibility of formations of closed orbits in the three-dimensional case.

The equations of motion are as follows. Let $r=\mathrm{OP}$ be the distance of the electron from O, the centre of the doublet, and θ the angle which OP makes with the axis of the doublet, and ϕ the angle which the plane POB makes with a fixed plane.

The equations of motion are

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta\dot{\phi}^2=-\frac{\mu}{r^2}-\frac{2\lambda\cos\theta}{r^3}, \quad . \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta\dot{\phi}^2=-\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad (2)$$

$$r^2\sin^2\theta\dot{\phi}=h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where λ is the strength of the doublet and is positive, μ is the constant of the central force and is either positive or negative, and h is constant.

There are three types of motion, which are to be considered separately :—

I. Motion on a right circular cone defined by $\theta=$constant.

II. Motion on a sphere defined by $r=$constant.

III. General motion, where all the coordinates vary.

I. MOTION ON A RIGHT CIRCULAR CONE.

Putting $\theta=\alpha$ (where α is constant) in the equations (1), (2), (3), we get the equations of motion to be

$$\ddot{r} - r\sin^2\alpha\dot{\phi}^2 = -\frac{\mu}{r^2} - \frac{2\lambda\cos\alpha}{r^3}, \quad . \quad . \quad . \quad (1)$$

$$r^4\dot{\phi}^2 = \lambda\sec\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$r^4\dot{\phi}^2 = h^2\operatorname{cosec}^4\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equations (2) and (3) are identical if

$$h^2 = \lambda\tan\alpha\sin^3\alpha.$$

Since h^2 is positive, we must have $0 < \alpha < \frac{\pi}{2}$. If $\alpha = 0$, then $h = 0$, *i. e.* the motion is along the line $\alpha = 0$; if $\alpha = \frac{\pi}{2}$, then the force perpendicular to r in the plane containing r and the axis of the doublet must vanish, i.e. r must be infinite, for λ is not equal to zero. In this case the motion is at infinity.

Circular Motion.

If $r = a$, where a is constant, the electron moves on a circle in a plane perpendicular to the axis of the doublet. In this case we have

$$\cos\alpha = -\frac{\mu a}{6\lambda} + \sqrt{\frac{\mu^2 a^2}{36\lambda^2} + \frac{1}{3}},$$

$$\omega^2 = \frac{\lambda}{a^4}\sec\alpha,$$

$$h = \pm a\sin^2\alpha\,\omega.$$

This is exactly the same case as that discussed on p. 42.

General Motion.

Eliminating $\dot{\phi}$ between (1) and (2), we get

$$\ddot{r} = -\frac{\mu}{r^2} + \frac{A}{r^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $$A = \frac{\lambda(3\sin^2\alpha - 2)}{\cos\alpha}.$$

The first integral of (4) is

$$\dot{r}^2 = \frac{2\mu}{r} - \frac{A}{r^2} + B, \quad . \quad . \quad . \quad . \quad (5)$$

where B is constant.

Thus the differential of the path is

$$\frac{1}{r^4}\left(\frac{dr}{d\phi}\right)^2=\frac{\cos\alpha}{\lambda}\left[\frac{2\mu}{r}-\frac{A}{r^2}+B\right].$$

Putting $u=\frac{1}{r}$, and writing $\frac{du}{d\theta}=w_1$, we get

$$u_1^2=\frac{\cos\alpha}{\lambda}\left[2\mu u-Au^2+B\right]. \quad . \quad . \quad . \quad . \quad (6)$$

The following cases are to be discussed separately —

(*a*) A positive.

(*b*) A zero.

(*c*) A negative.

CASE (*a*).—A positive, *i. e.* $\sin\alpha>\sqrt{\tfrac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1^2=\frac{A\cos\alpha}{\lambda}\left[\frac{B}{A}+\frac{\mu^2}{A^2}-\left(u-\frac{\mu}{A}\right)^2\right]$$

$$=\frac{A\cos\alpha}{\lambda}\left[\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2\right],$$

where $\frac{B}{A}+\frac{\mu^2}{A^2}=\frac{e^2}{l^2}$ and $\frac{\mu}{A}=\frac{1}{l}$.

Now $u_1=0$ at $u=\frac{1\pm e}{l}$.

If $e<1$, then r oscillates between the maximum and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively. In this case it is possible for periodic orbits to be formed.

If $e\geq 1$, then the maximum value of r is infinite. No periodic orbits exist in this case. Thus the path is always open.

The equation of the path is

$$\frac{l}{r}=1+e\cos\left[\left(\frac{A\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi+C\right], \quad . \quad . \quad . \quad (7)$$

where C is constant.

Periodic Orbits.

Let the initial conditions be $r=r_0$, $\phi=\phi_0$. The equation (7) becomes

$$\frac{l}{r}=1+e\cos\left[\cos^{-1}\left(\frac{l}{r_0}-1\right)/e-\left(\frac{\mathrm{A}\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi_0+\left(\frac{\mathrm{A}\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi\right].$$

For periodic orbits to be formed, we must have, in addition to $e<1$,

$$\left(\frac{\mathrm{A}\cos\alpha}{\lambda}\right)^{\frac{1}{2}}2k\pi=2m\pi,$$

i. e.

$$\frac{\mathrm{A}\cos\alpha}{\lambda}k^2=m^2,$$

where k and m are positive integers.

This condition gives

$$\sin\alpha=\sqrt{\frac{m^2}{3k^2}+\frac{2}{3}}.$$

The periodic orbits of the first order are given by $k=1$. It is obvious that they do not exist.

The periodic orbits of the second order are given by $k=2$. There is only one periodic order of that type, and that is given by $m=1$.

The periodic orbits of the third order are given by $k=3$. There are only two periodic orbits of that type, and these are given by $m=1$ and 2 respectively.

Similarly for orbits of higher order.

Thus we have established the existence of an infinite number of periodic orbits on the surface of a right circular cone.

(ii.) μ negative.

Put $\mu=\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1^2=\frac{\mathrm{A}\cos\alpha}{\lambda}\left[\frac{e^2}{l^2}-\left(u+\frac{1}{l}\right)^2\right],$$

where $$\frac{\mathrm{B}}{\mathrm{A}}+\frac{\mu'^2}{\mathrm{A}^2}=\frac{e^2}{l^2} \quad\text{and}\quad \frac{\mu'}{\mathrm{A}}=\frac{1}{l}.$$

If $e<1$, no motion is possible.

If $e=1$, the motion is altogether at infinity.

If $e>1$, r passes through the minimum value $\dfrac{l}{e-1}$ and then proceeds to infinity.

Thus no periodic orbits exist in this case.

The equation of the path is

$$\frac{l}{r}=-1+e\cos\left[\left(\frac{\mathrm{A}\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi+\mathrm{C}\right],$$

where C is constant.

Case (*b*).—$\mathrm{A}=0$, *i. e.* $\sin\alpha=\sqrt{\tfrac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1{}^2=\frac{\cos\alpha}{\lambda}\left[2\mu u+\mathrm{B}\right].$$

If B is positive, the electron goes to infinity if projected away from the origin, arriving there with a velocity $\sqrt{\mathrm{B}}$; but goes to the origin if projected towards it, arriving there with infinite velocity. Thus the path is always open.

The equation of the path is

$$\frac{1}{r}=\frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\alpha}\right)^{\frac{1}{2}}\phi+\mathrm{C}\right]^2-\frac{\mathrm{B}}{2\mu}.$$

If B is negative, then the maximum value of r is $\frac{2\mu}{\mathrm{B}'}$, where $\mathrm{B}'=-\mathrm{B}$. Thus the electron goes to the origin if projected away from or towards the origin.

The equation of the path is

$$\frac{1}{r}=\frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi+\mathrm{C}\right]^2+\frac{\mathrm{B}'}{2\mu}.$$

(ii.) μ negative.

Put $\mu=-\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1{}^2=\frac{\cos\alpha}{\lambda}\left[\mathrm{B}-2\mu' u\right].$$

Here B must be positive. The minimum value of r is given by $\frac{\mu'}{\mathrm{B}}$, after which the electron goes to infinity.

The equation of the path is

$$\frac{1}{r}\frac{\mathrm{B}}{2\mu}-\frac{1}{4}\left[\left(\frac{2\mu\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi+\mathrm{C}\right]^2.$$

CASE (*c*).—A negative, *i. e.* $\sin\alpha < \sqrt{\frac{2}{3}}$.

(i.) μ positive.

The differential equation of the path is

$$u_1^2 = \frac{A\cos\alpha}{\lambda}\left[2\mu u - Au^2 + B\right].$$

Put $A = -A'$, where A' is positive; then we get

$$u_1^2 = \frac{A'\cos\alpha}{\lambda}\left[\frac{B}{A'} - \frac{\mu^2}{A'^2} + \left(u + \frac{\mu}{A'}\right)^2\right].$$

Now, if $\frac{B}{A'} - \frac{\mu^2}{A'^2}$ is positive, we can put

$$\frac{B}{A'} - \frac{\mu^2}{A'^2} = \frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu'}{A} = \frac{1}{l}.$$

The differential equation of the path becomes

$$u_1^2 = \frac{A'\cos\alpha}{\lambda}\left[\frac{e^2}{l^2} + \left(u + \frac{1}{l}\right)^2\right].$$

In this case the radial velocity of the electron does not vanish and r does not oscillate. Thus no periodic orbits exist. If the electron is projected away from the origin it goes to infinity, but if projected towards the origin it arrives there.

The equation of the path is

$$\frac{l}{r} = -1 + e\sinh\left[\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi + C\right],$$

where C is constant.

If $B = \frac{\mu}{A'}$ the electron goes to the origin if projected toward it, but goes to infinity if projected away from the origin. Thus the path is always open and no periodic orbits exist.

The equation of the path is

$$\log\left[\frac{1}{r} + \frac{1}{l}\right] = C + \left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi,$$

where C is constant.

If $\frac{B}{A'}-\frac{\mu^2}{A'^2}$ is negative, then the differential equation of the path can be put in the form

$$u_1^2=-\frac{A'\cos\alpha}{\lambda}\left[\left(u+\frac{1}{l}\right)^2-\frac{e^2}{l^2}\right],$$

where $$\frac{B}{A'}-\frac{\mu^2}{A'^2}=-\frac{e^2}{l^2} \quad\text{and}\quad \frac{\mu}{A'}=\frac{1}{l}.$$

The equation of the path is

$$\frac{l}{r}=-1+e\cosh\left[C+\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi\right],$$

where C is constant.

If $e>1$ the maximum value of r is $\frac{l}{e-1}$, in which case the electron falls towards the doublet.

If $e<1$ the electron goes to infinity if projected away from the origin, but goes to the origin if projected toward it.

(ii.) μ negative.

Put $A=-A'$, where A' is positive,

and $\mu=-\mu'$, where μ' is positive.

The differential equation of the path is

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left[\frac{B}{A'}-\frac{\mu'^2}{A'^2}+\left(u-\frac{\mu'}{A'}\right)^2\right].$$

If $\frac{B}{A'}-\frac{\mu'^2}{A'^2}$ is positive, the differential equation of the path can be put in the form

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left[\frac{e^2}{l^2}+\left(u-\frac{1}{l}\right)^2\right],$$

where $$\frac{B}{A'}-\frac{\mu'^2}{A'^2}=\frac{e^2}{l^2}$$

and $$\frac{\mu'}{A'}=\frac{1}{l}.$$

The equation of the path is

$$\frac{l}{r}=1+e\sinh\left[C+\left(\frac{A'\cos\alpha}{\lambda}\right)^2\phi\right]$$

where C is constant.

This path is always open. The electron goes to infinity if projected away from the origin, but goes to the origin if projected towards it.

If $B=\frac{\mu'^2}{A'}$, the differential equation of the path is

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left(u-\frac{1}{l}\right)^2.$$

Thus the equation of the path is

$$\log\left(\frac{1}{r}-\frac{1}{l}\right)=C+\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi,$$

where C is constant.

This path is always open. No periodic orbits exist.

If

$$\frac{B}{A'}-\frac{\mu'^2}{A'^2}=-\frac{e^2}{l^2}\quad\text{and}\quad\frac{\mu'}{A'}=\frac{1}{l},$$

then the differential equation of the path is

$$u_1^2=\frac{A'\cos\alpha}{\lambda}\left[\left(u-\frac{1}{l}\right)^2-\frac{e^2}{l^2}\right].$$

In this case r has either the minimum value $\frac{l}{1-e}$ or the maximum value $\frac{l}{1+e}$, *i.e.* the motion is either outside $r=\frac{l}{1-e}$ and extends to infinity, or inside $r=\frac{l}{1+e}$, in which case the electron falls towards the doublet.

The equation of the path is

$$\frac{l}{r}=1+e\cosh\left[C+\left(\frac{A'\cos\alpha}{\lambda}\right)^{\frac{1}{2}}\phi\right],$$

where C is constant.

The path is always open and no periodic orbits exist.

II. MOTION ON A SPHERE.

From equations (1), (2), (3), p. 32, if we put $r=a$, where a is constant, we can derive the following equations:—

$$a^4\dot{\theta}^2=\mu a+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad (1)$$

$$a^4\dot{\theta}^2=A+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad (2)$$

$$a^2\sin^2\theta\dot{\phi}=h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A and h are both constant.

The equations (1), (2) are identical if $A=\mu a$. Thus the equations of motion on the surface of the sphere give rise to the following two equations :—

$$a^4\dot{\theta}^2=\mu a+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad (4)$$

$$a^2\sin^2\theta\,\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

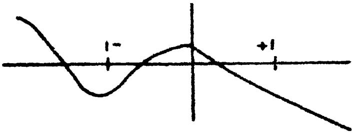
Putting $\cos\theta=x$, these equations become

$$a^4\left(\frac{dx}{dt}\right)^2=(\mu a+2\lambda x)(1-x^2)-h^2, \quad . \quad . \quad (6)$$

$$a^2(1-x^2)\frac{d\phi}{dt}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since the left-hand side of equation (6) is positive, the right-hand side must also be positive. Now, the right-hand side is a cubic polygonal in x; if $x=-\infty$ the cubic is positive; if $x=-1$ the cubic is negative; for some value of x between -1 and $+1$ the cubic must be positive; when $x=+1$ the cubic is again negative; and, lastly, when $x=+\infty$ the cubic is negative. The cubic has therefore two real roots between -1 and $+1$, and the third root is also real, but less than -1, so that it does not give a real value of θ.

Fig. 1.



Let the roots of the cubic be $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$, where $\cos\alpha>\cos\beta$.

The graphical representation of the cubic is as shown in the diagram (fig. 1).

Now, when

$$-\infty<x<-\cosh\gamma,$$

the cubic is positive but no real solution exists, for θ has no meaning;

$$-\cosh\gamma<x<\cos\beta,$$

the cubic is negative and no real solution exists;

$$\cos\beta<x<\cos\alpha,$$

the cubic is positive, in which case the motion is included between two cones of semi-vertical angles α and β respectively;

$$\cos\alpha < x < \infty,$$

the cubic is negative and no real solution exists.

Equation (6) can be put in the form

$$a^4\left(\frac{dx}{dt}\right)^2 = 2\lambda(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma),$$

where
$$\cos\alpha + \cos\beta - \cosh\gamma = -\frac{\mu a}{2\lambda},$$

$$-\cos\alpha\cos\beta + \cos\alpha\cosh\gamma + \cos\beta\cosh\gamma = 1,$$

$$\cos\alpha\cos\beta\cosh\gamma = \frac{h^2 - \mu a}{2\lambda}.$$

We see here that the cases where μ is positive or negative are not separable.

The differential equation of the path is

$$\frac{1}{1-x^2}\frac{dx}{d\phi} = \frac{(2\lambda)^{\frac{1}{2}}}{h}\{(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma)\}^{\frac{1}{2}}.$$

To integrate this equation put

$$x = \cos\alpha\cos^2\chi + \cos\beta\sin^2\chi,$$

where χ is a new variable.

With this substitution, the equation of the path is

$$\begin{aligned}\phi - \phi_0 = {} & \frac{h}{\sqrt{2\lambda(\cosh\gamma + \cos\alpha)}} \\ & \left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha - \cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi\right)\right. \\ & + \frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha - \cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi\right) \\ & - \frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha - \cos\beta}{1+\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi_0\right) \\ & \left. - \frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha - \cos\beta}{1-\cos\alpha}, \sqrt{\frac{\cos\alpha - \cos\beta}{\cosh\gamma + \cos\alpha}}, \chi_0\right)\right],\end{aligned}$$

where ϕ_0 and χ_0 are the initial values of ϕ and χ.

In the special case when $\alpha=\beta$ the motion is on the intersection of a cone of which the semi-vertical angle is given by

$$\cos\alpha=-\frac{\mu a}{6\lambda}+\sqrt{\frac{\mu^2a^2}{36\lambda^2}+\frac{1}{3}}$$

with a sphere. The motion in this case is circular. The angular velocity of the electron is given by

$$\omega^2=\frac{\lambda}{a^4}\sec\alpha,$$

and h is given by

$$h=\pm a\sin^2\alpha\;\omega.$$

This case is that usually known as steady motion, discussed on p. 33.

Periodic Orbits.

Periodic orbits are formed on the surface of the sphere if

$$\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\ \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\ k\pi\right)$$
$$+\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\ \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\ k\pi\right)=2n\pi,$$

where k and n are any positive integers.

Now, since

$$\cosh\gamma=\frac{1+\cos\alpha\cos\beta}{\cos\alpha+\cos\beta},$$
$$\frac{h}{\sqrt{2\lambda}}=\frac{\sin\alpha\sin\beta}{(\cos\alpha+\cos\beta)^{\frac{1}{2}}},$$

the condition for periodic orbits reduces to

$$\frac{\sin\alpha\sin\beta}{(1+2\cos\alpha\cos\beta+\cos^2\alpha)^{\frac{1}{2}}}\left[\frac{1}{1+\cos\alpha}\right.$$
$$\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\ \sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},\ k\pi\right)$$
$$+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\right.$$
$$\left.\left.\sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},\ k\pi\right)\right]=2n\pi. \quad . \quad (8)$$

In the equation (8) k is a definite quantity which determines the order of the orbits.

In general, assuming that real solutions exist, we can represent $\cos\alpha$ to be measured on the x-axis, $\cos\beta$ to be measured on the y-axis, in rectangular Cartesian coordinates. Having done this, we can equate each side to z, where z is a third coordinate perpendicular to the plane xy. Hence we get

$$z=2n\pi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

$$z=\left[\frac{(1-x^2)(1-y^2)}{1+2xy+x^2}\right]^{\frac{1}{2}}\left\{\frac{1}{1+x}\right.\Pi\left(-\frac{x-y}{1+x},\ \sqrt{\frac{x^2-y^2}{1+2xy+x^2}},\ k\pi\right)$$
$$\left.+\frac{1}{1-x}\Pi\left(\frac{x-y}{1-x},\ \sqrt{\frac{x^2-y^2}{1+2xy+x^2}},\ k\pi\right)\right\}. \quad . \qquad (10)$$

For different positive integral values of n the equation (9) represents a series of planes, and for a given positive integral value of k the equation (10) represents a surface. The intersection of (8), (9) is a series of curves on which the condition (8) is satisfied. If this intersection is real, then periodic orbits exist on the surface of the sphere. (Owing to the difficulty of obtaining tables, the condition (8) cannot be actually verified.)

The time is given by

$$t+\epsilon=\sqrt{\frac{2}{\lambda(\cosh\gamma+\cos\alpha)}}\,a^2\mathrm{F}\left(\chi,\ \sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right),$$

where ϵ is constant.

III. General Motion.

The equations of motion are

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta\dot{\phi}^2=-\frac{\mu}{r^2}-\frac{2\lambda\cos\theta}{r^3}. \quad . \quad . \qquad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta\dot{\phi}^2=-\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \qquad (2)$$

$$r^2\sin^2\theta\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

From (1), (2), (3) we can derive the following equations:—

$$\dot{r}^2=\frac{2\mu}{r}-\frac{A}{r^2}+B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$r^4\dot{\theta}^2=A+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where A and B are constants.

By a similar reasoning to that when the motion is on a sphere, we can show that the motion is included between two cones of semi-vertical angles α and β, where $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ are the roots of the cubic

$$A+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}=0.$$

Putting $\cos\theta=x$, we get the differential equations of the path to be

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=2\mu u-Au^2+B, \quad . \quad . \quad . \quad (6)$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}. \quad (7)$$

The following cases are to be discussed separately :—

(*a*) A positive.

(*b*) A zero.

(*c*) A negative.

CASE (*a*).—A positive.

(i.) μ positive.

The differential equations of the path are

$$\frac{2\lambda}{A}(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)},$$

where

$$\frac{e^2}{l^2}=\frac{B}{A}+\frac{\mu^2}{A^2},$$

$$\frac{\mu}{A}=\frac{1}{l},$$

$$\cos\alpha+\cos\beta-\cosh\gamma=-\frac{A}{2\lambda},$$

$$-\cos\alpha\cos\beta+\cos\alpha\cosh\gamma+\cos\beta\cosh\gamma=1,$$

$$\cos\alpha\cos\beta\cosh\gamma=\frac{h^2-A}{2\lambda}.$$

In the differential equations of the path put

$$x=\cos\alpha\cos^2\chi+\cos\beta\sin^2\chi;$$

then, after integrating, we get the equations of the path to be

$$\frac{l}{r}=1+e\cos\left[C+2\sqrt{\frac{A}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

$$\begin{aligned}\phi-\phi_0=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\Bigg[&\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\\&+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\\&-\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi_0\right)\\&-\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi_0\right)\Bigg],\end{aligned}$$

where C is constant, ϕ_0 and χ_0 are the initial values of ϕ and χ.

Now, if $e<1$, r oscillates between the maximum and minimum values given by $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively.

If $e \geq 1$, then the maximum value of r is infinite and the path is always open.

Periodic Orbits.

The conditions for periodic orbits are :

(i.) $e<1$ (this makes the value of r oscillatory);

(ii.) $$\sqrt{\frac{1-\cos^2\alpha-\cos^2\beta-\cos\alpha\cos\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}\,F\left(k\pi,\sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}}\right)=m\pi;$$

$$\text{(iii.)}\quad \frac{\sin\alpha\sin\beta}{(1+2\cos\alpha\cos\beta+\cos^2\alpha)^{\frac{1}{2}}}\Bigg[\frac{1}{1+\cos\alpha}\,\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},k\pi\right)$$
$$+\frac{1}{1-\cos\alpha}\,\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\right.$$
$$\left.\sqrt{\frac{\cos^2\alpha-\cos^2\beta}{1+2\cos\alpha\cos\beta+\cos^2\alpha}},k\pi\right)\Bigg]=2n\pi,$$

where k, m, n are any positive integers.

In equations (ii.), (iii.), k is a definite quantity which determines the order of the orbits.

In general, assuming that real solutions exist, we can represent $\cos\alpha$ to be measured along the x-axis, $\cos\beta$ to be measured along the y-axis in rectangular Cartesian coordinates. Having done this we can equate each side to z, where z is a third coordinate perpendicular to the plane of xy. Hence we get

$$z=m\pi, \qquad (8)$$

$$z=\left(\frac{1-x^2-y^2-xy}{1+2xy+x^2}\right)^{\frac{1}{2}}\mathrm{F}\left(k\pi,\sqrt{\frac{x^2-y^2}{1+2xy+x^2}}\right), \qquad (9)$$

$$z=2n\pi, \qquad (10)$$

$$z=\left[\frac{(1-x^2)(1-y^2)}{1+2xy+x^2}\right]^{\frac{1}{2}}$$
$$\left[\frac{1}{1+x}\Pi\left(-\frac{x-y}{1+x},\sqrt{\frac{x^2-y^2}{1+2xy+x^2}},k\pi\right)\right.$$
$$\left.+\frac{1}{1-x}\Pi\left(\frac{x-y}{1+x},\sqrt{\frac{x^2-y^2}{1+2xy+x^2}},k\pi\right)\right]. \qquad (11)$$

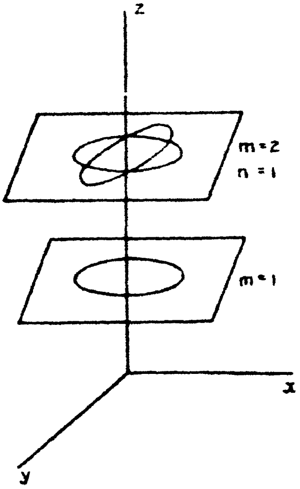
For any given positive integral value of k the equations (9), (11) represent two surfaces; and for different positive integral values of m, n the equations (8), (10) represent the two series of planes. The intersections of (8), (9) are a series of curves on which the condition (ii.) is satisfied; similarly the intersections of (10), (11) are a series of curves on which the condition (ii.) is satisfied. The graphical representation of these conditions is as shown in the diagram (fig. 2).

The points which give solution for periodic orbits are:—

(a) The points of intersection of the curves for which $m=2n$.

(*b*) Take any point on one of the "*m*" curves (*i.e.* 8, 9), draw a straight line from this point parallel to the z-axis; then if this straight line intersects one or more of the "*n*" curves (*i.e.* 10, 11), the values of $\cos\alpha$, $\cos\beta$ obtained is a solution for periodic orbits. This is simply because the point on the "*m*" curve and the points of intersection of the straight line through this point and parallel to the z-axis with the "*n*" curves give the same value of $\cos\alpha$, $\cos\beta$. In other words, project all the "*n*" curves on to the plane of any one of the "*m*" curves; then the points of intersection of this "*m*" curve and the projection of the "*n*" curves give solutions for periodic orbits.

Fig. 2.



It will be noticed that (*a*) is included in (*b*). (Owing to the difficulty of obtaining tables, the conditions (ii.) and (iii.) cannot actually be verified.)

(ii.) μ negative.

In equations (6), (7), p. 44, put $\mu = -\mu'$, where μ' is positive. These equations become

$$\frac{2\lambda}{A}(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma)\left(\frac{du}{dx}\right)^2 = \frac{e^2}{l^2} - \left(u + \frac{1}{l}\right)^2,$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{h^2}{2\lambda} \cdot \frac{1}{(1 - x^2)^2(\cos\alpha - x)(x - \cos\beta)(x + \cosh\gamma)}.$$

In this case, e must be greater than 1 for a real solution to exist. The maximum of r is infinite and the minimum value is $\frac{l}{e-1}$. In this case no periodic orbits exist.

The equations of the path are

$$\frac{l}{r}=-1+e\cos\left[C+2\sqrt{\frac{A}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

$$\phi+D=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

where C and D are constants and $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ have the same meaning as when μ is positive.

CASE (b).—A = zero.

(i.) μ positive.

The differential equations of the path are

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=2\mu u+B,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)},$$

where $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ are connected by the relations

$$\cos\alpha+\cos\beta-\cosh\gamma=0,$$

$$-\cos\alpha\cos\beta+\cos\alpha\cosh\gamma+\cos\beta\cosh\gamma=1,$$

$$\cos\alpha\cos\beta\cosh\gamma=\frac{h^2}{2\lambda}.$$

If B is positive, the electron goes to infinity if projected away from the origin, and goes to the origin if projected towards it. Thus the path in this case is always open.

Putting

$$x=\cos\alpha\cos^2\chi+\cos\beta\sin^2\chi,$$

the equations of the path are

$$\frac{4\lambda}{\mu}\cdot\frac{1}{r}+\frac{2\lambda B}{\mu^2}=\left[C+2\sqrt{\frac{1}{\cosh\gamma+\cos\alpha}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]^2,$$

$$\phi+D=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

where C and D are constants.

If B is negative, then r passes through the maximum value $\frac{2\mu}{B'}$, where $B=-B'$; thus the electron goes to the origin if projected away from or towards the origin. The equations of the path are as when B is positive, if we put $B=-B'$, where B' is positive.

(ii.) μ negative.

Put $\mu=-\mu'$, where μ' is positive.

The differential equations of the path are

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=-2\mu' u+B,$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\cdot\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}.$$

In this case B must be positive. Thus r passes through the minimum value $\frac{2\mu'}{B}$. The path is always open.

The equations of the path are

$$\frac{4\lambda}{\mu'}\cdot\frac{1}{r}=\frac{2\lambda B}{\mu'^2}-\left[C+\frac{2}{\sqrt{\cosh\gamma+\cos\alpha}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]^2.$$

$$\phi+\mathrm{D}=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}$$
$$\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

where C and D are constants.

CASE (*c*).—A negative.

Put $\mathrm{A}=-\mathrm{A}'$, where A' is positive.
The differential equations of the path are

$$2\lambda(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)\left(\frac{du}{dx}\right)^2=2\mu u+\mathrm{A}'u^2+\mathrm{B},$$

$$\left(\frac{d\phi}{dx}\right)^2=\frac{h^2}{2\lambda}\frac{1}{(1-x^2)^2(\cos\alpha-x)(x-\cos\beta)(x+\cosh\gamma)}.$$

(i.) μ positive.

If $\frac{\mathrm{B}}{\mathrm{A}'}-\frac{\mu^2}{\mathrm{A}'^2}$ is positive, the electron goes to infinity if projected away from the origin, but goes to the origin if projected towards it. Thus the path is always open.
The equations of the path are

$$\frac{l}{r}=e\sinh\left[\mathrm{C}+2\sqrt{\frac{\mathrm{A}'}{2\lambda(\cosh\gamma+\cos\alpha)}}\right.$$
$$\left.\mathrm{F}\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]-1,$$

$$\phi+\mathrm{D}=\frac{h}{\sqrt{2\lambda(\cosh\gamma+\cos\alpha)}}$$
$$\left[\frac{1}{1+\cos\alpha}\Pi\left(-\frac{\cos\alpha-\cos\beta}{1+\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right.$$
$$\left.+\frac{1}{1-\cos\alpha}\Pi\left(\frac{\cos\alpha-\cos\beta}{1-\cos\alpha},\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}},\chi\right)\right],$$

. . . (12)

where C and D are constants.

$$\cos\alpha+\cos\beta-\cosh\gamma=\frac{A'}{2\lambda},$$

$$-\cos\alpha\cos\beta+\cos\alpha\cosh\gamma+\cos\beta\cosh\gamma=1,$$

$$\cos\alpha\cos\beta\cosh\gamma=\frac{h^2+A'}{2\lambda},$$

$$x=\cos\alpha\cos^2\chi+\cos\beta\sin^2\chi.$$

If $B=\frac{\mu'}{A'}$, the path is always open.

The equations of the path are

$$\log\left(\frac{1}{r}-\frac{\mu}{A'}\right)=C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\;F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right),$$

and the equation (12).

If $\frac{B}{A'}-\frac{\mu^2}{A'^2}$ is negative, r passes through the maximum value $\frac{l}{e-1}$. If $e>1$ is greater than unity, the electron falls towards the doublet, but if e is less than unity, the electron goes to infinity when projected away from the origin, but goes to the origin when projected towards it.

The equations of the path are

$$\frac{l}{r}=e\cosh\left[C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\;F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right]-1,$$

and the equation (12).

(ii.) μ negative.

Put $\mu=-\mu'$, where μ' is positive.

If $\frac{B}{A'}-\frac{\mu'^2}{A'^2}$ is positive, the electron goes to infinity when projected away from the origin, but goes to the origin when projected towards it. Thus the path is always open.

The equations of the path are

$$\frac{l}{r}=1+e\sinh\left[C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

and equation (12), where C is constant.

If $B=\frac{\mu'}{A'}$, the path is always open.

The equations of the path are

$$\log\left(\frac{1}{r}-\frac{\mu'}{A'}\right)=C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right),$$

and equation (12), where C is constant.

If $\frac{B}{A'}-\frac{\mu'^2}{A'^2}$ is negative, then r either passes through the maximum value $\frac{l}{1+e}$ or the minimum value $\frac{l}{1-e}$. In the former case the electron falls towards the doublet, and in the latter case it goes to infinity. Thus the path is always open.

The equations of the path are

$$\frac{l}{r}=1+e\cosh\left[C+2\sqrt{\frac{A'}{2\lambda(\cosh\gamma+\cos\alpha)}}\,F\left(\chi,\sqrt{\frac{\cos\alpha-\cos\beta}{\cosh\gamma+\cos\alpha}}\right)\right],$$

and equation (12), where C is constant.

The author wishes to express his thanks to Prof. S. Brodetsky of Leeds University, under whose supervision the above work was done.

IV. *On the Change that a Gaseous Molecule may undergo between two Consecutive Collisions.* *By* R. D. KLEEMAN, *B.A., D.Sc.* *.

§ 1. *Introductory Remarks.*

IN a previous paper † the writer has shown that strictly according to thermodynamics the equation of a perfect gas is

$$pv=\xi\text{MRT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p denotes the pressure of a mass of M mols at the volume v and absolute temperature T, and ξ a function of the quantities T, v, and M. Under ordinary conditions the quantity ξ differs inappreciably from unity, but is less than unity when v is very large, as will be shown in § 2.

A consequence of this result and a previous investigation on the constant of mass action ‡ is that this constant under all conditions is likely to be appreciably a function of the volume and masses of the constituents as well as of the temperature, when the volume is very large. A corollary of this result is that a molecule during collision undergoes a physical and chemical change, or activation, which gradually disappears, on account of which the constant of mass action varies in this manner. In a subsequent article § some experimental evidence of this activation is discussed, which is shown, for example, by the effect of pressure on the spectrum of a gas. Another consequence of equation (1) is that contact catalytic action is likely to exist. The evidence in favour of this seems overwhelming, and will be considered in a separate article. In this paper the physical significance of the function ξ will be investigated.

§ 2. *The Function ξ Decreases as v Increases.*

On substituting in the well-known thermodynamical equation

$$\frac{\partial u}{\partial v}=\text{T}\frac{\partial p}{\partial \text{T}}-p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for p from equation (1), it becomes

$$\frac{\partial u}{\partial v}=\text{MR}\frac{\text{T}}{v}\frac{\partial \xi}{\partial \text{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[*] Communicated by the Author.

[†] Phil. Mag. v. p. 1191 (1928).

[‡] Phil. Mag. v. p. 263 (1928).

[§] 'Science,' lxviii. 1767, p. 459 (1928).

where u denotes the internal energy at the volume v and temperature T. On multiplying this equation by ∂v and integrating it between the limits ∞ and v, we obtain

$$u_\infty - u_v = \mathrm{MR}\int_v^\infty \frac{\mathrm{T}}{v}\frac{\partial \xi}{\partial \mathrm{T}} \cdot \partial v, \quad . \quad . \quad . \quad . \quad (4)$$

where u_∞ and u_v denote the internal energies of the gas at the volumes ∞ and v respectively. We may express ξ in the form of a sum of products of functions of T and v, or write

$$\xi = \Sigma\phi_1(\mathrm{T}) \cdot \phi_2(v). . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Each of the functions ϕ_2 may be expanded in a series of powers of v, or we may write

$$\phi_2(v) = \Sigma\frac{\mathrm{A}}{v^\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where α is a quantity at present unrestricted.

It is obvious that the left-hand side of equation (4) cannot be infinite. Therefore, if we substitute in the equation for ξ from equations (5) and (6), it appears that α can have only positive values integral or fractional. *It follows, therefore, that ξ decreases as v increases.* Another thermodynamical method of proving the existence of the function ξ and its properties will be given in § 5.

§ 3. *The Velocity of a Molecule in a Gas changes between two Consecutive Collisions.*

The function ξ, we have seen, decreases as v increases. On reflexion it will appear that this effect can be explained only by a decrease in the average velocity of translation of the molecules with increase of v. To see how this may come about, consider a rarefied gas from which some molecules are removed, keeping the volume constant. A decrease in the number of collisions per second, and in the velocity of translation of the molecules, simultaneously takes place, and hence we must look for an association between these two effects. If the velocity between two consecutive collisions of a molecule remained constant, the average velocity of the molecules would not decrease with the decrease in volume, or with decrease in the number of collisions. Hence we conclude that the velocity of a molecule gradually decreases after a collision, and that the subsequent collision increases it again to its initial value. The average velocity of the molecules will accordingly decrease with increase of volume.

The increase in velocity of a molecule during collision with another molecule can evidently take place only at the expense of the liberation of molecular internal energy, which has an effect resembling an explosion between the colliding molecules. This effect is appreciable only when the concentration is very small. Under ordinary conditions the change in the velocity of a molecule between two consecutive collisions, and the corresponding internal energy liberated, is inappreciable. The concentration at which this no longer holds must be determined by experiment (§ 6).

In general we may accordingly write

$$V_a - V_b = \phi(t), \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V_b denotes the velocity of a molecule before and V_a after collision, and t the time between two consecutive collisions. When t has a value smaller than that corresponding to a gas exceptionally rarefied, $\phi(t)$ is practically zero, and hence $V_a - V_b = 0$, approximately.

The value of V_a under the foregoing conditions is approximately that given by the equation

$$V_a = \sqrt{\frac{3RT}{m}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

derived from the orthodox gas theory, where m denotes the molecular weight of the gas. It may also hold in general down to the smallest concentrations, but it is scarcely likely; no theoretical prediction can be made at present in regard to this point. It may be pointed out that $V_a - V_b$ may be as small as we please, if the average velocity differs by an appropriate amount from that given by equation (8).

§ 4. *The Effect of Heat Radiation on the Molecular Velocity of Translation.*

The molecules of a gas cannot go on expending some of their internal energy while undergoing collisions without replenishing from some source. This, it seems, can be no other than the heat radiation surrounding the molecules. It is not difficult to conceive a process by means of which this replenishing may be brought about. The parts of two molecules nearest to each other during a collision most likely furnish the internal energy necessary to increase the molecular velocity after collision. These parts are therefore likely to be in a condition (after collision) to absorb radiant energy from the surrounding space, or to absorb more energy than they emit. In this manner the internal energy expended during a collision may wholly or partly be replenished in the interval between two consecutive collisions.

The parts diametrically opposite to the foregoing parts of two colliding molecules are in equilibrium with the surrounding radiation, and therefore they reflect as much radiation as they absorb. The pressure of the radiation on these parts would therefore be greater than on the former parts which absorb more than they reflect. The molecules would accordingly slow down under these opposing radiation pressures of different magnitudes. Thus the process that replenishes the internal energy expended during collision also gives rise to a decrease in the molecular velocity.

The average molecular velocity after a collision, or the average value of V_a, similarly as the total average velocity, probably depends on the molecular concentration as well as on the temperature, as has already been pointed out, and most likely decreases with decrease of concentration.

It can easily be shown that in general the radiation surrounding a molecule will affect its velocity of translation. Thus consider a molecule in equilibrium with the surrounding radiation, and suppose that its velocity, according to the orthodox view, remains unaltered when not undergoing a collision. Now suppose that the radiation surrounding the molecules is changed correspondingly to a different temperature. If the absorption and the reflexion of the heat radiation by the molecules are each changed by the same multiple over each part of the surface of the molecules, their average velocity of translation will remain unaltered. But since the average velocity is changed correspondingly to the temperature, it follows that the absorption and reflexion are changed in a way that each molecule is subjected to an asymmetrical radiation pressure which either increases or decreases its velocity, as the case may be. The corresponding radiant energy absorbed or emitted by the molecule per unit change in temperature, it may be pointed out, represents the internal molecular specific heat.

§ 5. *Another Method of deducing Equation* (1).

The effect of the pressure of a gas on its spectrum, and the effect of the concentration of a salt in a flame on its spectrum, shows that a molecule undergoes a physical change during collision which gradually disappears. This experimental fact will be used to deduce equation (1).

The foregoing change must necessarily be associated with a change in internal molecular energy, and hence the internal energy of a gas depends on its volume, or $\frac{\partial u}{\partial v}$ is not zero, where u denotes its internal energy. It follows, then, from equation (3) that ξ is a function of T. On completing the integration of equation (4), supposing ξ a function of T only, we obtain

$$u_{\infty}-u_v=\text{MRT}\frac{\partial \xi}{\partial \text{T}}\left\{\log \infty-\log v\right\} \quad . \quad . \quad (9)$$

where u_{∞} and u_v denote the internal energies of a gas at the volumes ∞ and v respectively. The right-hand side of the equation is infinite, and this should therefore also hold for the left-hand side. But this is impossible; and ξ is therefore a function of v as well as of T, which on integration of equation (4) renders the right side of the equation finite. This establishes equation (1) along a different line* of reasoning than before, and places its truth beyond doubt.

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* In a letter (Phil. Mag. vi. p. 743, 1928) the writer pointed out a thermodynamical proof of equation (1) which does not depend on the zero of entropy. Since this equation is of great importance, especially in connexion with mass-action, a complete outline of the proof will be given here. On writing Clapeyron's equation in the form

$$p(v_2-v_1)=\text{L}\frac{p}{\text{T}\frac{dp}{d\text{T}}-p},$$

the factor of L assumes an indeterminate form when $\text{T}=0$ and $p=0$, whose value is, however, finite and may be obtained by successive differentiations (J. Frank. Inst. 206 (5), p. 691, 1928). Therefore at $\text{T}=0$ we have $\text{L}=0$, since $p(v_2-v_1)=\text{RT}=0$. Now, suppose that a substance initially at $\text{T}=0$ under its vapour pressure is passed through the following cycle: (*a*) evaporate the substance, (*b*) raise the temperature of the vapour to T_m, (*c*) condense the vapour, (*d*) lower the temperature of the substance in contact with its vapour to $\text{T}=0$. On equating the change in internal energy to zero, and remembering that $\text{L}=0$, we obtain (*loc. cit.*)

$$\text{C}_{\infty}=\text{C}+\frac{\text{L}_m}{\text{T}_m},$$

where L_m denotes the internal heat of evaporation at T_m, and C_{∞} and C denote the average internal specific heats of the vapour and liquid respectively. Now it follows from thermodynamics that the scale of the perfect gas thermometer and the thermodynamical scale coincide if the ratio γ of the specific heats of the gas is a constant. But this does not hold for any substance according to the foregoing expression for C_{∞}, since L_m/T_m has a large maximum value when T_m is small. Hence if the scale of the gas thermometer is expressed in terms of the thermodynamical scale, equation (1) is obtained, where ξ is a function of the thermodynamical temperature T. It can then be shown from equation (9) in § 5 that it is also a function of the volume.

§ 6. *Experimental Methods of investigating the Nature of the Function ξ.*

The molecular concentration at which ξ begins to differ appreciably from unity cannot be predicted theoretically, but is probably extremely small. This point might be experimentally investigated by measuring the pressure of a rarefied gas by means of a device involving the velocity of molecular translation in its pressure formula, and comparing it with the pressure indicated by a device which measures the mass of a given volume of gas. A device of the latter kind is the McLeod gauge, but one of its drawbacks is that it cannot be used for very low pressures on account of the vapour-pressure of mercury. An ionization gauge might be found more convenient to use. The constants of both devices might be determined corresponding to a given pressure or pressures. On applying both devices to the measurement of the pressure of a rarefied gas which is gradually decreased by steps, a point will ultimately be reached when the pressure indicated by the device involving the velocity of molecular translation indicates a smaller value than the other. This point corresponds to the concentration at which ξ begins to deviate appreciably from unity. It will probably be found to depend on the nature of the gas.

§ 7. *Miscellaneous Deductions.*

(*a*) The exact form of the equation of state of a substance which conforms to equation (1) cannot be predicted theoretically at present. But forms may be suggested that might conceivably represent the facts. One of them referring to one mol is

$$p=\frac{\mathrm{RTA}}{v(va+1)}+\Sigma\frac{\mathrm{B}_\alpha}{v^{2+\alpha}}, \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

where α is a positive quantity equal to or greater than zero, and A, a, B_α are functions of T. Let us suppose that a is a very small fraction, say, of the order 10^{-5}, that A differs inappreciably from unity, and that B_α has values which render the summation expression in the equation negligible in comparison with the preceding term when v has values (per mol) corresponding to a gas under ordinary conditions. The equation of state of a gas under ordinary conditions is then

$$p=\frac{\mathrm{RT}}{v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

very approximately according to the foregoing equation, which agrees with experiment. When, however, the volume is infinitely large, the equation of state assumes the form

$$p=\left(\frac{\mathrm{RTA}}{a}+\mathrm{B}_1\right)\frac{1}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

according to which the pressure varies inversely as the square of the volume. The expression for ξ, according to equation (10), is therefore

$$\xi=\frac{\mathrm{A}}{av+1}+\frac{\mathrm{B}_1}{\mathrm{RT}v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we substitute for p in equation (2) from equation (10), multiply it by ∂v and integrate it between the limits of v and ∞, where v refers to a gas under ordinary conditions, it can easily be shown that very approximately

$$u_\infty-u_v=\mathrm{T}^2\frac{\partial}{\partial\mathrm{T}}\left\{\mathrm{RA}\ln\left(\frac{av+1}{av}\right)+\frac{\mathrm{B}_1}{\mathrm{T}v}\right\}. \quad . \quad . \quad (14)$$

The right-hand side is not infinite so far as the dependence of u on v is concerned, as should be the case since the left-hand side cannot be infinite.

(*b*) When a gas is very rarefied, the only force operating between the molecules is gravitational attraction. Now, Mills* has shown that when two molecules attract each other with a force varying inversely as the square of their distance of separation, the work w done in separating the molecules of a gram of substance at the volume v so that its volume is finally infinite, is given by

$$w=\frac{\mathrm{D}}{v^{\frac{1}{3}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where D is a constant. The intrinsic pressures P_n at the volume v, or the negative pressure due to the attraction of the molecules upon each other, is given by

$$\mathrm{P}_n=-\frac{\partial w}{\partial v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and hence

$$\mathrm{P}_n=\frac{\mathrm{D}}{3v^{\frac{4}{3}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The pressure p_t due to the motion of translation of the molecules is given by

$$p_t=\frac{\mathrm{RT}}{v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

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* J. Phys. Chem. viii. p. 383 (1904).

according to the orthodox view, and hence the pressure p actually exerted by the gas is

$$p_t - P_n = \frac{RT}{v} - \frac{D}{3v^{4/3}} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now, under ordinary conditions p_t is large in comparison with P_n, and this will still be the case however large the volume according to the right-hand side of the foregoing equation. Hence, if this equation were to hold, a mass of gas in interstellar space would continue to expand till evenly distributed.

But if p_t is given by equation (1), this may not take place. For example, if the pressure due to the motion of translation of the molecules of a gas whose volume is large is given by equation (12), it will follow that for a certain large volume $p_t - P_n$ is zero, and the gas will then cease to expand *as a whole* if left to itself. Under these conditions a gas in interstellar space would move like a solid body. These considerations may be of importance in interpreting the distribution and behaviour of masses of rarefied gases in interstellar space.

(*c*) It will be evident that Maxwell's law of distribution of molecular velocities holds only for a gas in which the velocities of translation of each molecule between two consecutive collisions does not change. When this no longer holds, the law has to be replaced by an appropriately modified form.

§ 8. *Applications to an Electron Gas.*

The case of an electron gas, or mass of matter consisting of electrons, requires special investigation. Consider a mass of electrons whose volume is increased till it is infinitely large, keeping the temperature at the absolute zero. The internal energy will evidently reach a limiting minimum value. According to a previous investigation *, this state corresponds to the zero of the controllable internal energy of the mass of electrons. It was also shown † that this zero lies on the adiabatic of zero controllable entropy. This particular adiabatic can be shown to correspond to $T=0$, since, according to our fundamental notions of heat, the specific heat is a positive quantity ‡, and hence an increase in temperature from $T=0$ will give rise to an increase in entropy. Therefore, if L denote the increase in internal energy and w the external work done on expanding the mass of electrons from the volume v to ∞ at $T=0$, we have

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* Phil. Mag. iii. p. 888 (1927).

† *Loc. cit.* iv. p. 261 (1927).

‡ *Loc. cit.* v. p. 668 (1928).

$$\frac{L+w}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now,

$$L+w=T\int_v^\infty \frac{\partial p}{\partial T}\cdot\partial v, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

according to equation (2), and hence, on combining the two equations, we have

$$\int_v^\infty \frac{\partial p}{\partial T}\cdot\partial v=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

at $T=0$.

The equation of state of a mass of gaseous electrons may be written

$$p=p_t-P_n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where p_t denotes the pressure the electrons exert due to their motion of translation, and P_n the intrinsic pressure due to the repulsion between the electric charges. p_t is given by equation (1) and P_n by equation (17) on changing the sign of the right-hand side, and the equation may therefore be written

$$p=\frac{RT\xi}{v}+\frac{D}{3v^{4/3}}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

On substituting from this equation for p in equation (22), it becomes

$$\frac{\partial}{\partial T}\left\{RT\int_v^\infty \frac{\xi}{v}\cdot\partial v\right\}=0. \quad . \quad . \quad . \quad (25)$$

Thus, unless ξ is an appropriate function of T, the left-hand side will not be zero. It can then be shown similarly, as in § 5, that ξ is also a function of v.

The various deductions made for an ordinary gas therefore also apply with slight modifications to an electron gas. One which is of particular interest is that an electron, like an atom, is *continually changing in nature*, though these changes may, of course, be immeasurably small. It appears, therefore, that the Universe has not only been evolving in respect to its shape and its animal and plant-life, but also in respect to the primordial electron and atom. That is perhaps just what we might expect. This aspect of the results obtained will be discussed in a special article.

An electron, like a molecule, undergoes a decrease in velocity between two consecutive collisions. But the process by means of which this is brought about is likely to be different in the two cases. When an electron absorbs radiant energy, this is likely to appear mainly as kinetic energy of translation. Let us suppose that this is so, and consider what happens when an electron is subjected to an alternating electric field. If the electron is moving parallel to the field with a velocity of its own, more work is done upon it when the field is acting in the same direction than when acting in the opposite direction. The electron would accordingly continually increase in velocity. This takes place also if the electron is subjected to fields whose axes lie in different directions, such as are furnished by the heat radiation surrounding it. But the velocity cannot continually increase, and therefore the force exerted on an electron by an electric field in the same direction as it is moving is less than when the field is acting in the opposite direction. Furthermore, since the electron should actually slow down if left to itself, the relation between these forces is such that this is brought about.

But the electron must also change in internal electronic energy, since its velocity is increased by a collision at the expense of this energy. It is difficult to see how this may be brought about according to our present knowledge of electricity. The electron is evidently, after all, an entity of some complexity; in fact, it seems safe to predict that it will be found very much so when we get to know a good deal more about its properties. These will be further investigated thermodynamically in connexion with radiation in a paper that will appear shortly.

§ 9. *Application to Carnot's Cycle.*

Since the laws of thermodynamics are, as far as we know, independent of the nature of matter, they will not be violated by a continuous change in the nature of matter with time, which the writer has predicted *, however great or small the change may be.

If Q_1 denote the heat taken in at the temperature T_1 in passing a substance through a Carnot's cycle, and Q_2 the heat given out at temperature T_2, the substance may repeatedly be passed through a cycle in which Q_1, Q_2, T_1, and T_2 have the same values. Since the substance continually changes in nature during the process, it is never the same as before at a point where an isothermal and an adiabatic curve of a cycle meet. Its internal energy need not be always the same either at such a point. But since the system as a whole may not continually loose or gain internal energy, the state corresponding to a given value of the internal energy is passed to a different point during each cycle without violating its thermodynamical laws.

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* Phil. Mag. v. p. 1191 (1928).

But this and other changes that take place in the physical properties of the substance, as may again be pointed out, are so small that they are of no practical importance; in fact, they are probably so small that they cannot be measured. The same remarks apply to the continual changes that take place in the chemical properties of a substance. But temporary changes may be induced in the atoms of a substance which give rise to a temporary and exceptionally pronounced departure in the chemical behaviour, as shown by the phenomenon of catalytic action.

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V. *The Limiting Density in White Dwarf Stars.*

By EDMUND C. STONER, *Ph.D.* (*Cambridge*), *Reader in Physics, University of Leeds**.

Introduction.

A NUMBER of stars are known whose calculated mean density is very much greater than that of any terrestrial matter. The classical example is the companion of Sirius. The mass of this star, as determined from the double-star orbit, is about ·85 that of the sun. It is a white star, its spectral type (A7) corresponding to an effective surface temperature of about 8000°. The luminosity, however, is very small, the absolute magnitude being 11·3. From the effective temperature and the absolute magnitude the radius can be calculated, and hence the mean density obtained. It is found to be about 50,000 gm./c.c. Stars of this type are classed as "white dwarfs," and although few are known with certainty, there is little doubt that they may be common objects in space, for, unless they were fairly near the sun, they would escape observation.

At the temperatures in the interior of stars atoms will be highly ionized, and if in white dwarfs the last stages of the process are reached, the atoms being broken up into nuclei and free electrons, there is no immediate difficulty in the existence of high densities. On a naïve view as to the "sizes" of electrons and nuclei (with radii some 10^{-5} times that of atoms) densities of the order of 10^{14} or 10^{15} would not be impossible.

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* Communicated by Prof. R. Whiddington, D.Sc., F.R.S.

Eddington* pointed out that on the usual classical theory a condensed star of the white dwarf type would not have sufficient energy to "cool down" to the ordinary uncondensed condition with unionized atoms. This paradox was cleared up by Fowler†, who applied the Fermi-Dirac statistics to matter at high densities. He found that the ultimate state was one in which the star was analogous to a gigantic molecule with only one configuration possible, and so effectively with temperature zero, and with no capacity for radiating, but none the less with a high energy.

In this paper a further application of the Fermi statistics will be made. The purpose is to discuss, under simplifying assumptions, whether there may be a limiting density due to the "jamming" of the electrons (owing to the exclusion principle which forms the basis of the Fermi statistics) independently of effects due to the appreciable size of any remaining incompletely ionized atoms.

Jeans‡ has put forward a remarkable and beautiful theory to account for the distribution of stars in the Russell temperature-luminosity diagram. Roughly, the tenanted portions of the diagram are supposed to correspond to stable states which are only possible when there are departures from the ideal gas laws in the stellar interiors; these behave as if in a "quasi-liquid" condition owing to the congestion of the atoms. The general idea may be indicated by a consideration of the process of shrinkage of a star associated with the radiation of energy and increase in temperature. Suppose the atoms to be ionized as far as the M-ring, leaving the K- and L-rings intact. The star will be unstable until the shrinkage has continued so far that there is a certain amount of "jamming" of the atoms (L-ring congestion). This will eventually be relieved by ionization due to increase of temperature, when another unstable state will set in, to be succeeded by the K-ring congestion state. Ionization of the K ring will lead to the white dwarf stage.

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* A. S. Eddington, 'The Internal Constitution of the Stars,' p. 172 (Cambridge Univ. Press, 1926).

† R. H. Fowler, "On Dense Matter," Monthly Notices of the R. A. S. lxxxvii. p. 114 (1926).

‡ J. H. Jeans, 'Astronomy and Cosmogony,' ch. v. (Cambridge Univ. Press, 1928).

About the last stage, Jeans says * : "In the white dwarfs the atoms are mainly ionized down to their nuclei, but a few K-ring atoms remain, and these, although few in number, probably occupy the major part of the available space; it is their jamming, rather than that of the nuclei, which results in the departures from the gas laws which ensure the stability of the star." It is in this connexion that there is considerable interest in the question as to whether there is a limit to electron "congestion" (using the word in the sophisticated sense already indicated) under the gravitational conditions in stars.

Approximate Calculation of Limiting Density.

The case of a sphere of uniform density of material composed of completely ionized atoms will be considered; the density increases as the sphere shrinks, and the limit will be reached when the gravitational energy released just supplies the energy required to squeeze the electrons closer together. The limiting case of high density occurs when the effective temperature is zero. (Compression necessitates addition of energy, for, since the phase-space is unchanged, and the volume is decreased, the limits of the momentum-space must be increased; in other words, the mean kinetic energy of the electrons must be increased.) The essential feature of the Fermi statistics applied to an assembly of free electrons is that not more than two electrons can occupy the same cell (of 6-volume h^3) in 6-dimensional phase-space. In the limit considered the cells occupied will be those corresponding to the lowest energies, and the mean kinetic energy per electron is then given by †

$$\frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3}\frac{h^2 n^{2/3}}{m},$$

where n is the number of electrons per unit volume. (This expression differs from that originally given by Fermi for *atoms*, being smaller by a factor $2^{2/3}$, necessitated by the statistical weight of the electron being 2, corresponding to its two orientations in a magnetic field.)

In fully ionized material the mean molecular weight is approximately equal to $2 \cdot 5\, m_H$ (m_H = mass of hydrogen atom) ‡. Let M be the mass of a sphere of radius r of uniform density.

$$M = \tfrac{4}{3}\pi r^3 (2 \cdot 5\, m_H n).$$

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* *L. c.* p. 156.

† See, for example, G. Birtwistle, 'The New Quantum Mechanics,' p. 243 (Cambridge Univ. Press, 1928).

‡ Jeans, *l. c.* p. 75.

Let N be the total number of "molecules" in the mass.

$$N = \tfrac{4}{3}\pi r^3 n = \frac{M}{2{\cdot}5\, m_H}.$$

The number of "molecules" is very nearly equal to the number of free electrons, and since the kinetic energy of the nuclei will be relatively small, the total kinetic energy E_K, to a close approximation, is given by

$$E_K = \frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3} \frac{h^2 n^{2/3}}{m} \cdot \frac{M}{2{\cdot}5\, m_H}.$$

The gravitational energy E_G is given by *

$$E_G = -aG\frac{M^2}{r},$$

where G is the gravitational constant, and $a = \frac{3}{5-n}$. The value of n depends on the distribution of density. For uniform density, the case here considered, $n=0$, so that $a = \frac{3}{5}$.

$$E_G = -\frac{3}{5}G\frac{M^2}{r} = -\frac{3}{5}\frac{GM^2(\frac{4}{3}\pi n)^{1/3}(2{\cdot}5\, m_H)^{1/3}}{M^{1/3}},$$

substituting the value of r in terms of M, n, and m_H.

The star will be able to contract, the released gravitational energy increasing the star's temperature until the energy given up is no longer sufficient to maintain the star at temperature zero; decrease in the volume occupied by the electrons necessitates an increase in their average momentum, and if the gravitational energy is insufficient for this, further contraction will be impossible. (The change in the negative electrostatic potential energy is neglected, as this for large densities will be small compared with the change in kinetic energy, as shown by an argument of Fowler †.) The condition for limiting density is given by

$$\frac{d}{dn}(E_K + E_G) = 0.$$

Writing

$$E_G = -\alpha n^{1/3}, \quad \text{where } \alpha = \frac{3}{5}GM^{5/3}(\tfrac{4}{3}\pi \times 2{\cdot}5\, m_H)^{1/3},$$

$$E_K = \beta n^{2/3}, \quad \text{where } \beta = \frac{3}{40}\left(\frac{3}{\pi}\right)^{2/3} \frac{h^2}{m}\frac{M}{2{\cdot}5\, m_H},$$

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* Eddington, *l. c.* p. 87.

† Fowler, *l. c.* p. 119.

n is a maximum when

$$\tfrac{1}{3}\alpha n^{-2/3} = \tfrac{2}{3}\beta n^{-1/3},$$

$$n = \left(\frac{\alpha}{2\beta}\right)^3.$$

Substituting the values of α and β,

$$n = 10^4\left(\frac{\pi}{3}\right)^3 \frac{G^3M^2{m_H}^4m^3}{h^6}.$$

Using the following values for the constants :—

$$G = 6{\cdot}66\times10^{-8}, \qquad m_H = 1{\cdot}662\times10^{-24},$$

$$m = 9{\cdot}01\times10^{-28}, \qquad h = 6{\cdot}55\times10^{-27},$$

this gives

$$n = 2{\cdot}31\times10^{-37}\,M^2,$$

or, expressing the mass as a fraction of that of the sum, $M_s(M_s = 2{\cdot}0\times10^{33})$,

$$n = 9{\cdot}24\times10^{29}\left(\frac{M}{M_s}\right)^2.$$

For the maximum density,

$$\rho = 2{\cdot}5\, m_H n$$

$$= 3{\cdot}85\times10^6\left(\frac{M}{M_s}\right)^2.$$

Discussion.

For the two white dwarfs for which most data are available, the following figures are quoted from Jeans :—

	M/M_s.	Spectrum.	T_e.	E.	r/r_s.	$\bar{\rho}$.
Sirius B…………	·85	A7	8,000	·007	·03	50,000
O_2 Eridani B…………	·44	A0	11,200	·002	·018	98,000

T_e is the effective surface temperature, deduced from the spectrum ; E the amount of energy radiated in ergs per gram, deduced from the total radiation (obtained from the absolute magnitude) and the mass ; r, the radius (given as a fraction of that of the sun r_s), can be found from T_e and the absolute magnitude. (For Sirius B, M/r has been found from the Einstein shift of spectral lines.) From r and M the mean density $\bar{\rho}$ may be calculated. Among other dense stars may be mentioned van Maanen's star ($\bar{\rho} > 100{,}000$,

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$E = \cdot001$, $r/r_s = \cdot009$) and Procyon B ($\bar{\rho}$ is probaby some tens of thousands, $E = \cdot0005$, $M/M_s = \cdot37$).

The mean densities will be much smaller than the central densities. If the gas laws were obeyed, for example, Eddington calculates* that the central density, ρ_c, of Sirius B would be about 3,000,000.

For uniform spheres of fully ionized matter of masses equal to those of Sirius B and O_2 Eridani, the calculation above yields the following values for the maximum limiting densities:—

For Sirius B......... $M/M_s = \cdot85$, $\rho_{\text{max.}} = 2\cdot77 \times 10^6$.

For O_2 Eridani B... $M/M_s = \cdot44$, $\rho_{\text{max.}} = 7\cdot48 \times 10^5$.

These values are of the same order of magnitude as those calculated for the central densities. Actually the stars are not at absolute zero, or they would not radiate at all, but the calculation remains approximately valid up to temperatures of the order of some million degrees, because the assembly of free electrons at these high concentrations will remain an almost completely degenerate system. (Sommerfeld's degeneracy criterion †, $\frac{nh^3}{2} \cdot \frac{1}{(2\pi mkT)^{3/2}} > 1$, gives with $n = 10^{30}$, $T < 3\cdot5 \times 10^9$: with $n = 10^{27}$, $T < 3\cdot5 \times 10^7$.) These considerations suggest that in white dwarfs there is a central portion in which most of the mass is concentrated, and whose density approaches the limiting value; and that this central portion is surrounded by a more diffuse layer, the condensed state gradually changing into the ordinary ionized gas state as the edge of the star is approached.

The radius ($r_{\text{min.}}$) of a completely condensed star of mass M may be readily obtained:

$$\tfrac{4}{3}\pi r^3_{\text{min.}}\,\rho_{\text{max.}} = M.$$

Writing r_s, M_s, and ρ_s for the radius, mass, and mean density of the sun ($\rho_s = 1\cdot42$),

$$\left(\frac{r_{\text{min.}}}{r_s}\right)^3 = \frac{M}{M_s}\,\frac{\rho_s}{\rho_{\text{max.}}}.$$

This gives, as the values of $\frac{r_{\text{min.}}}{r_s}$ for Sirius B, $\cdot0075$, and for O_2 Eridani B $\cdot011$, as compared with the values of $\frac{r}{r_s}$ of $\cdot03$ and $\cdot018$. It would appear that O_2 Eridani B has much more nearly approached the completely condensed condition, which is in keeping with its smaller radiation per gram than that of Sirius B (·002 as compared with ·007 erg).

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* Eddington, *l. c.* p. 174.

† A. Sommerfeld, *Zeits. f. Phys.* xlvii. p. 1 (1928).

On this view the central portion would be in a practically incompressible state, and so would be in the "quasi-liquid" condition which Jeans postulates as essential to the stability of stars. The essential point is that such a condition of congestion can be brought about solely on account of the "space requirements" of the electrons, and that it is not necessary to assume that there is any "jamming" of a few remaining K-ring atoms.

Similar phase-space considerations, however, do nothing to clear up the difficulties in Jeans's theory in connexion with more ordinary stars. In order that there should be the necessary deviations from Boyle's law in matter at the densities and temperatures deduced for the central regions, the effective volumes of the atoms (ionized down to the K, L, M ... rings, according to the conditions), must be much greater than that suggested by the orbital theory of the atom *. The space-charge distribution model of the atom does not greatly change the estimates of atomic "sizes," as is seen by an inspection of the curves given by Hartree † for Rb^+. If, following Thomas ‡, the phase-space method is used for obtaining a rough estimate of the volume occupied by electrons in atoms, values of the same order of magnitude are obtained.

For Jeans's liquid-star theory it is not only necessary that the sizes of incompletely ionized atoms should be much greater than those estimated, but also that the volume "required" by an atom with, say, all its L-electrons just before the temperature is great enough to ionize the L-ring should be much larger than the volume required by the L-ionized atom, together with the free L-electrons, after ionization. Phase-space consideration suggests that there should be little change in the required volume.

The fact that there are these difficulties does not, of course, necessarily invalidate Jeans's general explanation of the non-uniformity of distribution of stars in the temperature-luminosity diagram. Rather its inner coherence is so striking as to suggest that there are other unknown or unrecognized factors to be considered on the atomic theory side.

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* Jeans, *l. c.* p. 159.

† D. R. Hartree, Proc. Camb. Phil. Soc. xxiv. p. 111 (1928).

‡ L. H. Thomas, Proc. Camb. Phil. Soc. xxiii. p. 542 (1927).

Summary.

Using the Fermi statistics, it is shown that, under the influence of gravitational and electron "packing" effects, the limiting density ρ of a uniform sphere of mass M, consisting of a mixture of fully-ionized atoms, is approximately given by

$$\rho=3{\cdot}85\times10^6\left(\frac{M}{M_s}\right)^2,$$

where M_s is the mass of the sun.

For spheres with tho masses of Sirius B and O_2 Eridani B the limiting densities are $2{\cdot}8\times10^6$ and $7{\cdot}5\times10^6$.

It is suggested that white dwarfs contain a core of material approaching the limiting density, the ratios of the radius of the core to the radius of the star, in the two cases considered, being about ·25 and ·61. The core will be in an almost incompressible or "quasi-liquid" state, due to the "congestion" of the electrons.

Jeans's theory of the distribution of stars in the Russell temperature-luminosity diagram is briefly discussed. It is shown that the quasi-liquid state required for stability may be attained in white dwarfs owing simply to electron-packing, without the necessity of assuming "jamming" of the few remaing K-ring atoms.

Physics Department,
The University, Leeds.
October 1928.

VI. *Radiometer Effect of Positive Ions.* *By* CHAS. T. KNIPP, *Ph.D., Professor of Experimental Electricity, University of Illinois, and* WESLEY S. STEIN, *M.A.*[*]

I. *Introduction.*

THE rolling of a Crookes mica mill-wheel in a vacuum by a beam of cathode rays is a well-known phenomenon. As to the nature of the force exerted, J. J. Thomson [†], after calculating the possible force due to change of momentum of the particles upon impact, concluded that the "movement is probably due to an effect similar to that observed in a radiometer, as the impact on the vanes will make one side of the vanes hotter than the other." Starke [*] showed this to be the case by using the apparatus in which the radiometer effect was eliminated. He suspended a flat disk by a fine wire fastened at the centre of the disk. A beam of cathode rays was directed against the bottom of the disk near its outer edge and at an angle of 45° with the vertical and with the tangent to the disk at the point of incidence. The arrangement, being comparatively insensitive to vertical forces, was not affected by the radiometer effect nor by the vertical component of the direct mechanical force. The horizontal component should produce a rotation. Starke found no sensible deflexion, thus proving that the direct mechanical effect, due to a beam of cathode rays, was below the sensitivity of his instrument, which was 10^{-4} dyne.

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[*] Communicated by the Authors.

[†] J. J. Thomson, Cond. Elec. through Gases, 2nd ed. p. 630.

The corresponding phenomenon in the case of positive rays is not so well known, and no conclusive data seem to have been taken to show whether the force exerted by a beam of positive rays is a secondary effect, as in the case of cathode rays, or whether the force is purely mechanical.

Swinton [†] observed the rotation of wheels having mica and aluminium vanes, respectively, when placed in the path of positive rays. In the case of mica vanes he measured the difference in temperature between the sides of the vane. The maximum temperature difference observed was 200° centigrade. He also observed that the greatest speed of rotation took place when the difference in temperature was the greatest, and hence concluded that the effect was a secondary or radiometer effect.

The purpose of the present investigation has been to study still further the nature of the force exerted by a positive ray beam, and to arrive, if possible, at a more satisfactory explanation of the phenomenon.

II. *Theory.*

If we know the kind of ions which compose the beam; and also their velocity and the number striking the vane per second, it is possible to predict the direct mechanical force due to the beam when the ions lose all their momentum upon striking the vane. In the present experiment the gas in the tube was residual air, and it is also known that under the conditions of this experiment most of the positive ions are atomic in size and singly charged. Also, the error introduced into the calculated value of the force by the presence of some molecular ions will tend to cancel that introduced by the presence of a number of doubly-charged ions in the beam. We may then assume singly-charged atomic ions. There are usually a few negatively-charged ions in the positive-ray beam, the presence of which would make the calculated value of the force a little too low. This error helps to counteract the error due to the fact that not all the positive ions have a velocity as great as that corresponding to the total potential drop across the tube, which is the only value available for use in the calculations. The error due to the use of the total potential drop in the calculations is probably the only one which might be large enough to seriously affect the validity of the result.

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[*] Starke, *Ann. d. Phys.* iii. p. 101 (1900).

[†] Swinton, Proc. Roy. Soc. lxxix. p. 391 (1907).

Keeping in mind the foregoing conditions, we may write

$$1/2mv^2 = Ve,$$

where m is the mean atomic weight for air and was taken to be 14·4. All quantities are measured in electromagnetic units. Then

$$v = \sqrt{\frac{2Ve}{m}}.$$

The momentum of a single ion travelling with the velocity v is accordingly

$$mv = \sqrt{2Vem}.$$

When an ion is stopped by the vane, assuming it is not reflected, the change of momentum will also be

$$\sqrt{2Vem}.$$

But from Newton's second law

$$F = \frac{d}{dt}(mv).$$

In this case the rate of change of momentum is equal to n (the number of ions striking the vane per second), multiplied by the momentum which each ion loses upon impact. Hence

$$F = n\sqrt{2Vem}.$$

But
$$n = \frac{i}{e};$$

therefore F may be written

$$F = i\sqrt{\frac{2Vm}{e}}.$$

If i is measured by a galvanometer and V by a calibrated spark-gap, the value of F is known. This formula applies only when the direction of the beam and the direction of motion of the vane coincide. When the angle between the two directions is θ the value above must be multiplied by $\cos\theta$. The general formula is then

$$F_{\text{obs.}} = i\sqrt{\frac{2Vm}{e}}\,.\cos\theta.$$

To calculate the actual force of the beam from measurements of the twist in the suspension, it is necessary to find the amount of force applied to the vane which is required to cause a twist of the suspension through one radian. Using the formula for the torsion pendulum,

$$T = 2\pi\sqrt{\frac{I}{c}},$$

we have an expression for c, the constant of torsion, in terms of T the period and I the moment of inertia. To find T and I a piece of aluminium, of weight comparable to the weight suspended while in use and of such shape that its moment of inertia could easily be calculated, was suspended and the period of the pendulum found. Hence

$$c = \frac{4\pi^2 I}{T^2},$$

where T and I are known. To find F it is merely necessary to divide by the length of the lever-arm. Hence

$$F_{\text{calc.}} = \frac{c}{d} = \frac{4\pi^2 I}{T^2 d}.$$

This is the force which has to be applied to the vane to twist the suspension through one radian. The twist being measured, the total force can be found.

III. *Apparatus.*

The first type of apparatus used in this investigation was basically a Knipp-Kunz * positive-ray tube having a shutter in front of the positive-ray orifice and a side-tube allowing a thin aluminium vane to be inserted across the path of the positive-ray beam. The cathode was a hollow aluminium cylinder 2·5 cm. in diameter and 5 cm. long, completely closed except for a 3-mm. hole at the centre of each end. The shutter was mounted upon a brass rod pivoted upon a tungsten point, and could thus be grounded. The shutter itself was made of two parts. One was of thin microscope cover-glass, which cut off the rays but permitted light from the discharge to pass through and fall upon the vane. The other part was of thin aluminium, which cut off both the ions and the light. A fine silver suspension was used at first, but this was found to be too delicate. It was replaced by a phosphor-bronze strip. Its length was 25 centimetres. The vane was a thin sheet of aluminium 2 cm. square, mounted vertically upon one end of an aluminium cross-bar. The apparatus was so designed that the cross-bar and vane could be inserted into the side-tube and hooked to the suspension by a hook at the back of the mirror. The inside of the tube containing the cross-bar as well as that part of the discharge-tube containing the vane were lined with aluminium foil in order to shield the suspended system from electrostatic effects. The shielding metal and shutter were grounded.

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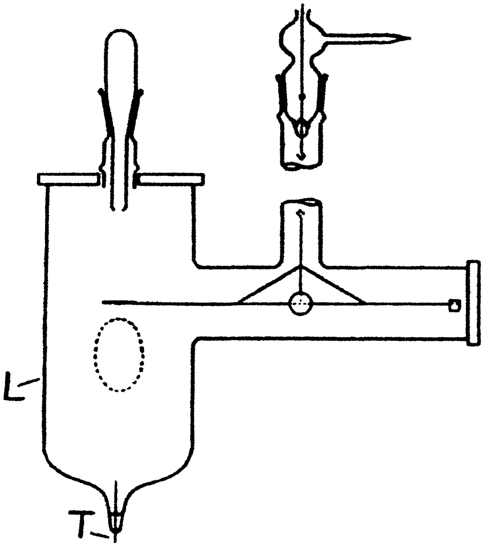
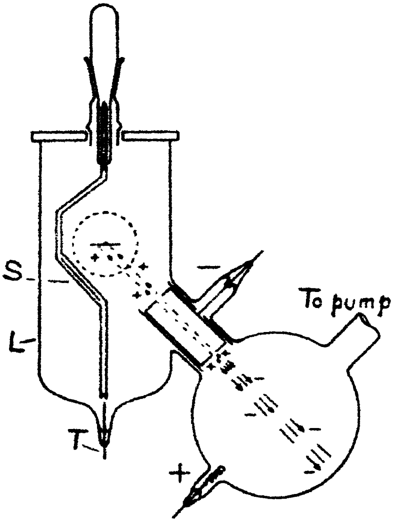
* Knipp, Trans. Ill. Acad. Sci. x. p. 283 (1918).

Fig. 1.



The type of apparatus described above is suitable for measuring the force caused by a positive-ray beam, but does not discriminate between direct mechanical force and a secondary radiometer effect. Hence the apparatus shown in figs. 1 and 2 was finally constructed. It operates on the same principle as that used by Starke referred to earlier in-this paper. It differs from the first apparatus mainly in that the vane is mounted in an horizontal position and that the rays strike it from below at an angle (fig. 2) of 45°. The shutter S is shown swung out of line of the positive-ray beam. To overcome any dissymmetry of the beam, the cathode was enclosed in a separate glass collar (also shown in fig. 2) which extended far enough to protect the beam from the effects of the unsymmetrical location of the glass caused by the 45° junction. The tubes containing the cross-bar and suspension were made larger than in the first apparatus in order to facilitate the insertion of the suspended system. The chamber L was closed at the top by a glass plate, a feature which made the insertion of the shutter and shielding easy. These were grounded through T. This apparatus was constructed of Pyrex glass beakers and Florence flasks.

Fig. 2.



A sensitive galvanometer was used to measure the current to the vane, and the potential across the tube was measured by a sphere-gap. At first centimetre spheres were used, but these were replaced by a calibrated sphere-gap between spheres 12·5 cm. in diameter. This gap, which was made by the Victor X-ray Supply Company of Chicago, has a screw adjustment and scale which made possible quite accurate readings.

IV. *Observations.*

The electric wiring connected the shutter and shielding to ground, and also connected the suspended system to ground through the galvanometer. With the first apparatus the cross-bar was centred as nearly as possible along the axis of the tube and let come to rest. Then, with the aluminium shutter interposed, the discharge was started and the cross-bar observed. It was found that the only movement which occurred was a slight irregular shifting, the direction of which depended upon the direction the cross-bar happened to be off centre at the time the discharge was started. This procedure was then repeated with the glass shutter and the same results obtained. These trials were repeated at various times, always with similar results. Hence the effect due to the light from the discharge was less than 10^{-4} dyne.

In making observations of the force exerted by the beam, the equilibrium position was noted with the discharge running and the shutter closed. The shutter was then opened and the torsion head rotated sufficiently to bring the cross-bar back to the same position. The precaution of balancing the cross-bar with the shutter closed and the discharge running was for the purpose of eliminating the effect of the spurious drift described above, which seemed to depend upon the position of the balance. The number of degrees of rotation necessary to bring back the cross-bar was read off on a scale fastened at the torsion head. The pressure, galvanometer deflexion, and potential drop across the tube were also recorded. Since it was impossible to take all readings simultaneously, it was necessary to make observations only when the conditions remained fairly constant. It was found necessary to use a weak magnetic field to deflect all electrons from the beam in order to get the true value of the positive current.

Typical data obtained with the first apparatus by the procedure outlined above are included in Tables I. and II.

The procedure in making observations with the second tube was similar to that used with the first. However, since the deflexions of the vane were quite small in this case, it was found better not to turn the torsion head, since it was liable to set the vane swinging, but to read the deflexion directly from marks placed on the plate glass at the end of the cross-bar opposite the vane. In reading a position the observer always sighted along the end of the cross-bar and the vertical suspension. Because of the small size of the

TABLE I.

Galv. Deflex. (mm.).	Vane Deflex. (degrees).	Potential (volts).	Pressure (mm. Hg).
18·5	35	30,000	·00030
16·5	25	30,000	·00028
18·5	33	30,000	·00029
19·5	40	30,000	·00030
19·0	42	30,000	·00029
18·8	41	30,000	·00029
17·5	37	30,000	·00030

$F_{\text{calc.}} = {}$·0149 dyne.

$F_{\text{obs.}} = {}$·0143 dyne.

TABLE II.

Galv. Deflex. (mm.).	Vane Deflex. (degrees).	Potential (volts).	Pressure (mm. Hg).
25·0	21	30,000	·00034
31·0	46	30,000	·00030
29·0	44	30,000	·00028
34·0	40	30,000	·00028
28·5	34	30,000	·00029
33·0	34	30,000	·00029
32·5	34	30,000	·00027
36·5	36	30,000	00029
36·5	35	30,000	·00024

$F_{\text{calc.}} = {}$·0145 dyne.

$F_{\text{obs.}} = {}$·0140 dyne.

TABLE III.

Galv. Deflex. (mm.).	Vane Deflex. (mm.).	Potential (volts).	Pressure (mm. Hg).
7·0	7·0	18,000	·00028
6·5	5·0	17,000	·00034
7·0	7·0	17,500	·00032
6·5	7·5	17,500	·00030
7·0	7·5	18,000	·00032
7·0	8·0	18,000	·00024
7·0	7·5	17,500	·00026
6·5	8·0	18,000	·00026

$F_{\text{calc.}} = {}$·0017 dyne.

$F_{\text{obs.}} = {}$·0012 dyne.

deflexions observed with the second type of apparatus, it was imperative that the needle should be allowed to become very quiet before an observation was made. Typical data obtained by the second method are given in Tables III. and IV.

The values for $F_{calc.}$ which are recorded in the above two tables were calculated in the same manner as in Tables I. and II., except that in the latter case θ was 45 degrees.

V. *Discussion of Results.*

Although the data obtained by the first method led to values of $F_{obs.}$ which agree very well with $F_{calc.}$, yet nothing is proven by the close agreement, since we do not know what percentage of the force is due to a radiometer effect and what to direct mechanical effect; however, the results do suggest a probable slowing-down of the rays by the residual air in the tube. This, as may be seen by averaging the values in Tables I. and II., amounts for the particular pressure used to about 4 per cent.

TABLE IV.

Galv. Deflex. (mm.).	Vane Deflex. (mm.).	Potential (volts).	Pressure (mm. Hg).
14·5	10·0	12,000	·00132
13·5	6·0	12,000	·00108
15·0	9·0	10,000	·00090
16·0	6·0	13,000	·00082
17·5	6·0	12,500	·00082
18·0	6·0	13,000	·00078
19·0	8·0	13,000	·00078

$F_{calc.} = \cdot 0033$ dyne.

$F_{obs.} = \cdot 0013$ dyne.

The fact, however, that a measurable force was detected with the second apparatus is important, since it shows that, contrary to what was previously thought, at least a part of the bombardment of a beam of positive rays results in a direct mechanical effect. By referring to Table III., in which the radiometer effect is eliminated, it is seen that the observed values of F are about 29 per cent. lower than the calculated values; *i. e.*, the value of the direct mechanical effect, in this instance, is 71 per cent. of the value calculated on the theory given in section II. of this paper. These two values are not corrected for the slowing-down of the rays due to the presence of residual air This residual-air effect is the same in Table III. as it is in Tables I. and II., since the pressure was kept approximately constant. It is a question how to proportion this correction between the radiometer and mechanical effects. We have tentatively assumed it to be in the ratio of 1 : 4. Hence, taking the residual-air effect as 4 per cent., we may write radiometer effect 28 per cent., and mechanical effect 68 per cent. These data are shown under I. and II., also III., in Table V. Apparently the proportion between radiometer and mechanical effects depends also upon the material and thickness of the vane. In this case the vane was ·1 mm. thick and the pressure was ·0003 mm. of mercury.

A glance at Table IV. reveals the fact that pressure has a marked effect upon the results. With the pressure at ·0009 mm. Hg the rays were slowed down sufficiently so that their actual force on the vane was only about 39 per cent. of the calculated value. Here, again, it is difficult to state the results definitely. Assuming that the radiometer effect is the same as in Table III. (which assumption is open to question), the distribution may be set down roughly as in IV. of Table V.

TABLE V.

Table	Radiometer and Mechanical Effect. (%).	Radiometer and Residual-Air Effect. (%).	Radio-meter Effect. (%).	Residual-Air Effect. (%).	Mechanical Effect. %).	Total.
I. & II. (averaged).	*96*	?	?	*4*	?	100
III. ...	96	29	*28*	*4*	*68*	100
IV.......	67	60	*28*	*32*	*39*	99

It is the intention of the writers to collect additional data over a considerable range of pressures with both the first and second types of apparatus in order to arrive more nearly at the exact magnitude of the various effects, and also how they vary. All calculations were made on the assumption that the positive ions are not reflected when they strike a grounded vane. This should also be tested experimentally.

Laboratory of Physics,
University of Illinois.
June 15, 1928.

VII. *The Dispersion of Double Refraction in Quartz.*

By F. C. HARRIS, *M.Sc.*, *University College, London* *.

[Plate I.]

IN connexion with some recent researches in photo-elasticity, a pair of left-handed quartz wedges, arranged as a parallel plate whose thickness could be varied by sliding one wedge over the other, were used to measure the retardation produced in bodies under pressure. It became necessary therefore to investigate the dispersion of double-refraction in the quartz for a much larger number of wave-lengths throughout the visible spectrum than had been done by previous investigators, and it was with this object that the research here described was carried out.

The two quartz wedges, placed together as a parallel plate, cut parallel to the optic axis, were mounted on the "prism table" of a spectroscope in such a way that they could be rotated as a whole plate about this optic axis.

Light from a Point-o-Lite lamp passed horizontally through the plate—*i. e.*, perpendicular to the optic axis. The plate was situated between crossed nicols, and an image of it was focussed by a lens on the slit of a Littrow spectrograph, as in fig. 1 (Pl. I.).

The image seen in the camera of the spectrograph consisted of a continuous spectrum crossed by a number of vertical black bands. By means of a small reflecting prism and a shutter, a comparison spectrum of the iron arc was obtained on either side of the "banded" spectrum, as in fig. 2 (Pl. I.).

The quartz plate was carefully adjusted so that the light passed normally through it, and a photograph of the bands and comparison spectrum was taken. This photograph was then carefully measured on a Hilger plate-measuring machine and the wave-length of the middle of each band determined.

To find the order of any particular band, the comparison spectrum was removed and replaced by a sodium flame, and also the camera was replaced by a telescope. By rotation of the plate about the optic axis, a band could be brought into coincidence with the sodium lines. The angles of rotation required to bring bands of successive orders into such coincidence with the sodium lines were determined, and from these observations the order n of the band nearest the sodium lines at normal incidence was calculated from the following well-known formula :—

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* Communicated by Prof. L. N. G. Filon, F.R.S.

$$\text{Time retardation} = \frac{t}{v_0}\{\mu_1 \cos r_1 - \cos i\} = \tau_1,$$

where t = thickness of plate,

v_0 = velocity of light in air,

i = angle of incidence,

r_1 = angle of refraction for the ordinary ray,

μ_1 = ordinary refractive index.

Now,

$$\mu_1 \cos r_1 = \sqrt{\mu_1^2 - \sin^2 i}.$$

For the ordinary ray $\quad \tau_1 = \frac{t}{v_0}\{\sqrt{\mu_1^2 - \sin^2 i} - \cos i\},$

Similarly,

For the extraordinary ray $\tau_2 = \frac{t}{v_0}\{\sqrt{\mu_2^2 - \sin^2 i} - \cos i\}.$

The time retardation between the ordinary and extraordinary rays due to a thickness t of the quartz

$$= \tau_2 - \tau_1 = \frac{t}{v_0}\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}.$$

The equivalent retardation in centimetres of air

$$= v_0\tau_2 - v_0\tau_1 = t\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}.$$

Now, if λ is the wave-length of any band of order n for normal incidence,

$$n\lambda = t(\mu_2 - \mu_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If a rotation i is now made which brings the band of order $(n+p)$ on to the same wave-length λ, we have

$$(n+p)\lambda = t\{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}\}, \quad . \quad (2)$$

and from (1) and (2) we get

$$\frac{(n+p)\lambda}{n\lambda} = 1 + \frac{p}{n} = \frac{\sqrt{\mu_2^2 - \sin^2 i} - \sqrt{\mu_1^2 - \sin^2 i}}{\mu_2 - \mu_1}$$

$$= \frac{\mu_2^2 - \mu_1^2}{(\mu_2 - \mu_1)\{\sqrt{\mu_2^2 - \sin^2 i} + \sqrt{\mu_1^2 - \sin^2 i}\}}$$

$$= \frac{\mu_2 + \mu_1}{\sqrt{\mu_2^2 - \sin^2 i} + \sqrt{\mu_1^2 - \sin^2 i}}.$$

If successive bands are now brought into coincidence with the sodium lines as above, p has the values 1, 2, 3, ... etc.

Hence, substituting the measured values of i, and taking the values of μ_1 and μ_2 from those of Gifford* for the particular wave-length $\lambda=5893$, a series of approximate values of n is obtained.

But n is known to be an integer, and hence n can be determined exactly. Thus Gifford's value of $\mu_2-\mu_1$ is only used to give an indication of the order n, the actual results obtained being independent of his values.

The procedure is then as follows:—

Let the band nearest the sodium lines be of order n. Rotate the plate to bring this band into coincidence with the cross-wire of the telescope, which has previously been set on one of the sodium lines. Let the angle of rotation from the normal be i_1.

Then

$$n\lambda = t\{\sqrt{\mu_2{}^2-\sin^2 i_1}-\sqrt{\mu_1{}^2-\sin^2 i_1}\}.$$

Rotate further, so that the band of order $n+p$ is on the cross-wires. Let the angle of incidence be i_2.

Then

$$(n+p)\lambda = t\{\sqrt{\mu_2{}^2-\sin^2 i_2}-\sqrt{\mu_1{}^2-\sin^2 i_2}\}.$$

From these last two equations we have

$$1+\frac{p}{n}=\frac{\sqrt{\mu_2{}^2-\sin^2 i_2}-\sqrt{\mu_1{}^2-\sin^2 i_2}}{\sqrt{\mu_2{}^2-\sin^2 i_1}-\sqrt{\mu_1{}^2-\sin^2 i_1}}.$$

If $p=1$,

$$1+\frac{1}{n}=\frac{\sqrt{\mu_2{}^2-\sin^2 i_1}+\sqrt{\mu_1{}^2-\sin^2 i_1}}{\sqrt{\mu_2{}^2-\sin^2 i_2}+\sqrt{\mu_1{}^2-\sin^2 i_2}}.$$

Repeat measuring angles i_3, i_4, etc. ... for values of $p=2$, 3, 4, ... etc.

A series of values of n will thus be obtained from which the true value—*i. e.*, the integer—is determined.

For the particular plate used the values of n thus found were 77·36; 77·06; 77·08; 77·01; 77·11; 76·98; 76·80; 76·83; 76·93; 76·92. Obviously the integral value of n was 77.

Having determined n for one particular band, the orders of all the other bands in the spectrum are known.

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* Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).

Now for any band at wave-length λ.

$$\text{Total retardation} = n\lambda = t\,.\,\phi(\lambda),$$

where $\phi(\lambda)$ is the value of $\mu_2-\mu_1$ at wave-length λ.

$$\therefore \quad \phi(\lambda) = \frac{n}{t}\,.\,\lambda.$$

By assuming the value of $\phi(\lambda)$ as obtained by previous investigators for one particular wave-length, the thickness of the plate t can be calculated, and hence the value of $\phi(\lambda)$ at any other wave-length λ can be determined.

The value of $\phi(\lambda)$ used here was taken from Gifford's values for $\lambda=5899{\cdot}693$,—this being the wave-length of the band of order 76,—and this gave the thickness $t=4{\cdot}92224$ mm. A measurement of t by a micrometer screw-gauge reading to $\frac{1}{1000}$ inch gave $t=4{\cdot}94$ mm.

Hence, t being known, the values of $\phi(\lambda)$ for these wave-lengths corresponding to successive bands throughout the spectrum, as measured from the photograph, could now be calculated. This was done for 57 bands, the results being given in the following table :—

Table of Values of $\phi(\lambda)=\mu_2-\mu_1$ for Quartz.

Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.	Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.
7116·052	0·008963	(6438	0·009044)
(7066	0·008987)	{6437	0·00897}
7011·289	0·008974	6365·149	0·009052
6910·607	0·008985	6282·488	0·009062
6813·913	0·008998	6200·737	0·009070
6719·078	0·009009	6122·355	0·009080
(6708	0·009013)	[6076	0·009077]
6626·274	0·009019	6047·303	0·009091
(6563	0·009017)	5971·898	0·009099
6536·735	0·009030	*5899·693	0·009109
6448·948	0·009040	(5893	0·009110)

Observations due to other investigators :—

( ) Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).
{ } Sarasin, 'Smithsonian Tables,' table 193.
[ ] Ehringhaus, *Neues Jahrbuch d. Mineralogie*, xli. p. 342 (1916).

Table of Values of $\phi(\lambda)=\mu_2-\mu_1$ for Quartz (*cont.*).

Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.	Wave-length λ.	$\phi(\lambda)=\mu_2-\mu_1$.
{5892	0·00916}	4775·735	0·009314
5829·057	0·009119	4732·166	0·009325
5760·898	0·009129	4689·460	0·009337
5693·799	0·009138	{4676	0·00934}
5628·602	0·009148	4647·716	0·009348
(5607	0·009144)	4606·722	0·009359
5565·090	0·009158	4566·303	0·009370
5502·912	0·009167	4527·330	0·009382
(5461	0·009171)	4488·601	0·009393
5441·799	0·009176	4450·784	0·009404
5383·916	0·009188	[4415	0·009403]
{5377	0·00918}	{4414	0·00952}
{5336	0·00920}	4413·691	0·009415
5326·492	0·009198	4377·600	0·009427
5270·296	0·009208	(4359	0·009430)
(5270	0·009211)	4341·844	0·009438
5216·043	0·009219	(4341	0·009430)
5162·573	0·009230	4307·265	0·009451
5110·306	0·009240	4272·822	0·009462
[5097	0·009235]	4239·575	0·009474
{5084	0·00924}	4206·520	0·009486
5059·233	0·009250	4174·244	0·009498
5009·171	0·009261	4142·426	0·009510
4960·026	0·009271	4111·544	0·009522
4912·644	0·009282	4080·534	0·009533
4866·063	0·009293	[4054	0·009536]
(4861	0·009288)	4050·927	0·009547
4820·469	0·009304	(4046	0·009560)
(4800	0·009317)	4021·096	0·009558
{4799	0·00929}	3992·265	0·009571

Observations due to other investigators:—

( ) Gifford, Proc. Roy. Soc. A, lxx. p. 329 (1902), and lxxxiv. p. 193 (1910).

{ } Sarasin, 'Smithsonian Tables,' table 193.

[ ] Ehringhaus, *Neues Jahrbuch d. Mineralogie*, xli. p. 342 (1916).

Comparing the results of $\phi(\lambda)=\mu_2-\mu_1$, obtained by the present method, with those of previous investigators, it will be seen that:—

(a) *Gifford.* Present values agree within the limits of experimental error, throughout the whole table, with the exception of the extreme values, and even here the disagreement is not appreciable.

(b) *Sarasin.* In general, the agreement is very poor throughout, and at $\lambda=6437$, 5892, and 4414, the difference between the two sets is far greater than could possibly be accounted for by experimental errors.

(c) *Ehringhaus.* The present values are all slightly greater than these, but the difference between the two sets is practically constant throughout.

The agreement with Gifford is not surprising since the present determinations have been adjusted, as explained above, to give the same value at the particular wave-length $\lambda=5899{\cdot}693$. The discrepancies between the values now obtained and those of Sarasin are also to be expected, for the values of μ_2 and μ_1 given by Gifford and Sarasin respectively, differ appreciably, whereas there is fairly good agreement between the values given by Gifford and Ehringhaus.

The almost complete agreement between the present values and those of Gifford and Sarasin indicate that the law of dispersion of double refraction is sensibly identical in different specimens of quartz.

In conclusion, I should like to record my very sincere thanks to Prof. L. N. G. Filon, F.R.S., for his great help and encouragement throughout the progress of this research.

[*Note.*—A further measurement of the thickness t, by weighing the plate first in distilled water and then in air, correcting for pressure and temperature, gave the value 4·9124 mm.]

VIII. *The Action of Ionizing Radiations on Colloids.* By J. A. Crowther, *M.A., Sc.D., F.Inst.P., Professor of Physics in the University of Reading* *.

§1. *Preliminary.*

It has been shown, in previous communications from this laboratory (1, 2, 3), that positively-charged colloids are affected by exposure to X-radiation. Lyophobic sols, such as a Bredig solution of copper, are precipitated by the radiation; lyophilic sols, such as ceric hydroxide, show first a rapid decrease in viscosity followed by a rise in viscosity with ultimate setting to a gel. We have suggested as a cause for these phenomena the gradual discharge of the charged colloidal particles by the ionization produced in the solution by the passage of the rays.

On this hypothesis it is to be expected that other ionizing agents, such as the beta-rays from radium, would produce similar results. Such an effect had, in fact, been already demonstrated for one or two lyophilic sols, in particular by Hardy (4) for positively-charged globulin solutions, and by Fernau and Pauli (5) for the ceric hydroxide sol. These experiments were qualitative rather than quantitative, and it was thought that a direct quantitative comparison between the effects of the two types of radiation would not be without interest. If the observed effects were due to the production of ions in the sol, they should depend only on the number of ions produced, and not upon the agent used for producing the ions. They would thus provide an additional test of this hypothesis.

The sols selected for the experiment were (*a*) a ceric hydroxide sol, (*b*) a Bredig solution of copper. The methods adopted for preparing these sols and investigating their behaviour under X-rays have been sufficiently described in previous communications, and were followed out without change in the experiments now to be described. Certain modifications in the procedure had to be made when exposing the sols to the beta-rays, as the intensity of the radiation, even from a strong radium source, is small in comparison with the output of an X-ray tube, and it was undesirable to prolong the time of exposure unduly.

The source of beta-radiation was a small thin-walled glass bulb, 0·95 cm. in diameter, containing initially rather more than 100 millicurie of radium emanation, which was very kindly supplied for the experiment by Prof. S. Russ, and the first operation was to measure the ionization produced by the beta-rays from this source in the ionization chamber employed in all our experiments for the measurement of the X-radiation. As it was undesirable to move either the X-ray tube or the ionization chamber, the emanation tube was clamped immediately in front of the window of the X-ray tube, it having been ascertained that at this distance the beta-rays would pass through the ionization chamber without falling directly on either of the electrodes. The ionization current in the chamber was then measured, using a Wilson electroscope and a suitable known capacity (0·0051 mf.). The aperture of the ionization chamber was then closed with a sheet of lead, and the ionization current, due now to the gamma-radiation only, was again measured. The difference between the two currents measured the ionization due to the beta-rays alone. The distance of the emanation bulb from the window of the ionization chamber was then measured, and the bulb removed.

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* Communicated by the Author.

We can now calculate the total charge which would pass across the ionization chamber during an exposure of, say, one hour, at a definite time, and at a definite standard distance, which in the actual experiment was 8·3 cm. It was found that the beta-ray current under these circumstances was 0·091 microcoulomb per hour. Since the emanation decays exponentially with the time, it is a simple matter to calculate the charge for an exposure of one hour at any later date, or, perhaps more simply, to calculate what length of exposure at the time when the ionization measurements were made is equivalent to an exposure of one hour at some later date. The times of exposure in this paper are all given in terms of this standard.

§2. *Experiments with Ceric Hydroxide Sol.*

The sol used in the experiments was of the type denoted by S/4 in the previous paper(2). As the exposures to X-rays followed exactly the procedure described in detail in that communication, it is unnecessary to describe them further here. The viscosity of the sol after exposure to a measured dose of X-rays was compared with the viscosity of a second sample of the same sol which had been treated in exactly the same manner as the first except for the exposure to the rays. The percentage change in viscosity produced by the exposure is thus measured and plotted against the dose, as measured by the total charge in microcoulombs (mc.) which passed through the ionization chamber during the exposure. The results, as might be expected, showed exactly the same general features as those described in the earlier work. It was, however, necessary to make the observations afresh, as the numerical values vary with the age of the sol.

The exposures to beta-radiation were made with the same stock of sol, and were carried on simultaneously with the X-ray measurements. The method of exposure was, however, different. A small volume (1 c.c.) of the sol was placed in a rather large quartz test-tube with a hemispherical end. The bulb containing the emanation was supported centrally in the tube, so that exactly half the bulb was immersed in the sol, which then just filled the hemispherical end of the quartz tube. The tube was securely sealed during the exposure. The times of exposure varied from about twenty minutes up to three hours. The percentage change in viscosity was determined at the end of the exposure in exactly the same way as in the X-ray experiments.

The results of these two sets of experiments are given in Table I. The durations of the beta-ray exposures have been reduced to standard time, as previously explained. They are shown graphically in fig. 1, where the full curve with the crosses represents the X-ray results, and the broken curve and circles the beta-ray measurements. From these curves we can draw up a table comparing the amounts of X-ray exposure (in mc.) and beta-ray exposure (in hours) required to produce the same percentage change in the

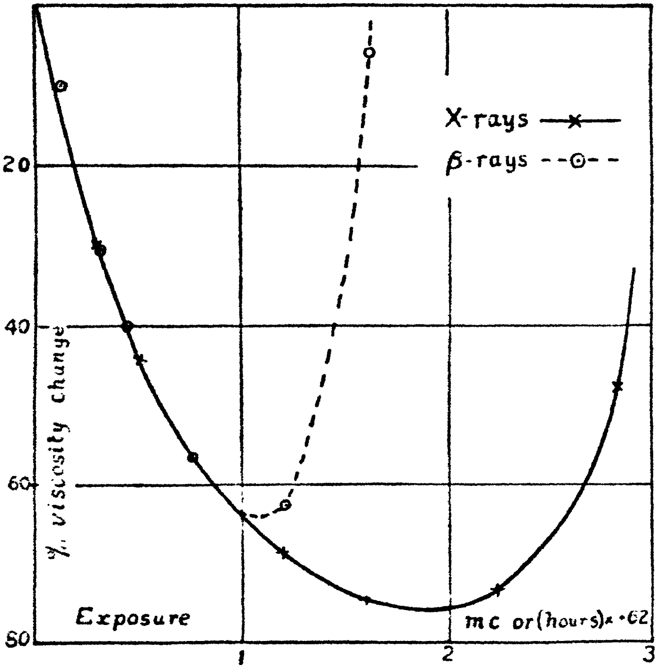
TABLE I.

Effect of X- and β-rays on the Viscosity of a Cerium Sol.

X-radiation.		β-radiation.	
Dose in mc.	Per cent. decrease in viscosity.	Exposure in hours.	Per cent. decrease in viscosity.
·30	30·0	·25	7·3
·50	44·5	·50	30·6
1·20	68·5	·74	40·0
1·60	74·5	1·22	56·8
2·24	73·9	1·95	62·2
2·84	48·1	2·60	5·8

viscosity of the sol. The figures are given in Table II It will be seen from the last column of this table that these exposures bear a ratio to one another which is constant up to a change in viscosity of 60 per cent. Thus, if we reduce

Fig. 1.



Changes in viscosities of ceric hydroxide sol with varying exposures to X- and β-rays.

TABLE II.

Equivalent X- and β-ray Exposures for a Cerium Sol.

Per cent. change in viscosity.	X-ray dose in m.c.	β-ray dose in hours.	hours. / mc.
−20	0·18	0·31	·58
−30	0·30	0·48	·62
−40	0·43	0·70	·61
−50	0·62	1·00	·62
−60	0·86	1·38	·62

the abscissæ of the dotted curve in the ratio of 0·62 to 1, the first portion of the beta-ray curve will lie almost exactly on that for X-rays. This is shown by the circles on this curve.

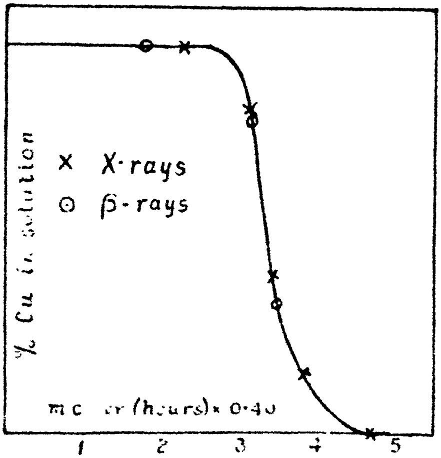
If we follow Smoluchowski and assume that the increased viscosity of a viscous solution is due to the charges carried by the colloidal particles, it follows that the first portion of the viscosity-dosage curves represent the gradual discharge of the particles by the radiation employed. The increase in viscosity which follows is due to the aggregation of the particles, which are no longer kept apart by their mutual electrical repulsion. There is no doubt that the radiation plays some part in this aggregating process. We have found, for example, that a cerium sol which has had its viscosity reduced to the minimum value by exposure to X-rays will remain fluid for at least 24 hours if the exposure is discontinued, but will set to a firm gel if the exposure is continued for another half hour, and effects of the same kind are also shown when beta-rays are used. The curves in fig. 1 might thus be interpreted as showing that there is a numerical equivalence between the action of X-rays and that of beta-rays as far as the discharge of the colloidal particles is concerned, but that the aggregating powers of the two types of radiation are different.

The latter conclusion is, however, hardly justifiable on the experimental evidence, for two reasons. In the first place the exposures to beta-radiation occupy a considerably longer time than the X-ray exposures, so that the process of aggregation, which proceeds at a definite rate, has a greater chance to come into play. A second disturbing factor lies in the difference in absorbability of the two kinds of radiation. Rather less than half the X-radiation was absorbed in the thickness of sol used in the experiments, but nearly 90 per cent. of the beta-radiation was absorbed. The layers nearest the emanation bulb would thus be exposed to radiation ten times more intense than those furthest away, an effect which would be still further accentuated by the geometry of the apparatus. While diffusion and convection would no doubt do much to neutralize this inequality, it seems probable that when the discharge of the particles was approaching completion those close to the emanation tube would become completely discharged, and being in an intense stream of radiation aggregate rapidly, before those which were further away had lost all their charge. The mean viscosity of the liquid would thus be appreciably increased, and would never fall to the value indicating complete discharge. The question as to the equivalence of the coagulating effects must therefore be regarded as open. What the experiments do show clearly is that there is a constant ratio between the quantity of X-rays and the quantity of beta-rays required to produce a given decrease in viscosity in the sol.

§ 3. *Experiments with Colloidal Copper.*

Similar experiments were carried out with a Bredig solution of copper. As this sol is very sensitive to minute traces of contaminating substances, the beta-ray exposure was made in the same way as the X-ray exposure; that is to say, in a quartz dish hermetically sealed under a glass cover-slip. The emanation bulb was simply placed on the cover-slip. The effect of the radiation was estimated by measuring the percentage of copper remaining in solution after exposure. The two curves in this case coincide exactly, within the limits of experimental error, as shown in fig. 2, where the crosses indicate X-ray and the circle beta-ray exposures. The scale of abscissæ have, of course, been chosen to bring the two curves into coincidence at one point.

Fig. 2.



Percentage of copper remaining in solution after exposure to varying does of X- and β-rays.

The experiments with copper are not affected by the conditions which complicated those with the cerium sol, since a copper particle, when discharged, is simply precipitated, and the time element does not come into account. These experiments bring out very clearly the equivalence between the discharging effects of the two types of radiation.

A further set of experiments was made in which cerium sol was exposed under conditions identical with those used for the copper sol, with a view to ascertaining whether either of the sols showed any selective effect towards the two kinds of radiation. It was found that with this disposition of the emanation tube an exposure of one hour to the beta-rays was equivalent to a dose of 0·39 mc. of X-rays. For the copper sol, under identical circumstances, an exposure of one hour to the beta-rays produced the same effect as a dose of 0·40 mc. of X-radiation. The ratio of the beta-ray to the X-ray effects is thus independent of the nature of the solution within the limits of experimental error.

§ 4. *The Relative Energy expended by X-rays and Beta-rays in the Sol.*

The final step in the comparison between the action of X-rays and beta-rays on the colloid is some estimation of the relative energy expended by each in the sol. Thus, assuming that with the arrangements adopted in the earlier section of the paper an exposure of one hour to the emanation is equivalent to a dose of 0·62 mc. of X-rays, how do the energies absorbed in the sol during these equivalent exposures compare?

It is possible to make this comparison if we assume that the energy spent in producing a pair of ions in air is the same for both types of radiation, an assumption for which there is some experimental evidence. Our experiments showed that at the standard time the beta-rays from the emanation allowed the passage through the ionization chamber of 0·091 microcoulomb of charge. The distance of the emanation tube from the window of the chamber was, however, only 8·3 cm. as compared with 10·75 cm. for the source of the X-radiation. If the emanation tube had been placed in the same position as the focus of the X-ray tube, the charge passing through the chamber in one hour would have been $0{\cdot}091 \times \left(\frac{8{\cdot}3}{10{\cdot}75}\right)^2$, or 0·054 mc. Allowing for the absorption of the beta-rays in the air between the emanation tube and the chamber, which amounted to 6 per cent., we arrive finally at the value of 0·058 mc. per hour.

For beams of different absorbability the relative ionization currents do not give an immediate comparison of the energies of the beams. It is necessary to take into account also the relative absorptions. The ionization method of comparing the energies of heterogeneous beams of radiation has been discussed in detail in a recent paper by Dr. Bond and myself(6), and it is unnecessary to recapitulate the argument. It can be shown that the only reliable comparison is provided by the total ionization produced by the complete absorption of the beam. The total ionzation is given by the expression $\frac{I_0}{\Delta_m} \cdot \alpha$, where I_0 is the measured ionization in a volume of gas of which Δ_m is the mass per unit area, and α is the area of the absorption curve for the radiation in air, or some equivalent substance. If the energy spent per ion in air is constant, this expression is a measure of the energy of the beam.

Assuming a uniform distribution of radiation round the source, the energy passing into the sol is proportional to the solid angle Ω subtended by it at the radiator. Of this only a fraction f is absorbed, the remainder being transmitted. The energy absorbed in the sol is thus given by

$$k \frac{I_0 \alpha}{\Delta_m} \cdot f \cdot \Omega,$$

where I_0 is the charge collected by the ionization chamber during the exposure, and k is a constant.

To evaluate this expression it is necessary to obtain absorption curves for the radiation in air, and in the sol. The measurement of the absorption curves for air for the X-ray beam was described in an earlier paper(6). For the beta-radiation the absorption curve was measured with water as the absorbing substance, as the direct measurement of the absorption curve for air presented great experimental difficulties. This substitution appears to be justifiable in the case of beta-radiation, since its mass absorption coefficient differs very little for elements of low atomic number. Absorption curves were also determined for the sols employed, from which the values of f could be determined.

Turning now to the experiments on the ceric hydroxide sol of § 2, the solid angle subtended at the focus of the X-ray tube with the dish at a distance of 3·2 cm. was 0·205. The corresponding angle in the case of the beta-ray exposure was taken as 2π. This seems to be justifiable from the symmetry of the arrangements. Experimentally an exposure to X-radiation which liberates 0·62 mc. in the ionization chamber is equivalent in its effects on the solution to one hour exposure to beta-radiation, which in turn would have produced a charge of 0·058 mc. in the chamber. The mass of air in the chamber is the same for both. So also is the constant k, if we assume that the energy required to produce a pair of ions in air is the same for X-rays and beta-rays, an assumption which seems probable and for which there is some experimental evidence (6).

The necessary data are collected in Table III. The last column of the table contains the relative energies of the two kinds of radiation required to produce the same decrease in viscosity of the cerium sol. It will be seen that they agree to an accuracy of about 6 per cent. This is certainly within the limits of our possible experimental error. Thus, to this degree of accuracy, we conclude that the energy which must be absorbed in a given volume of sol to bring about a given loss of charge by the colloidal particles within it is independent of the nature of the ionizing radiation. The results described in § 3 clearly enable us to extend this conclusion to the copper sol.

The effect of the gamma-radiation has not been taken into account in the calculations. It must, however, be quite small. The energy of the gamma-radiation is known, from the thermal measurements, to be about twice that of the beta-radiation. Its coefficient of absorption in water is, however, so small that the energy absorbed from it in the sol would not amount, at most, to more than one per cent. of its total energy, and its effect must therefore be very small. Its effect, if any, would be to increase the energy expended in the sol during the beta-ray exposures, and thus to bring the two results into closer agreement. To insert a correction of this order of magnitude, however, would give the experiments an air of accuracy to which they can lay no claim.

TABLE III.

	I_0	a.	f.	Ω.	Relative energy.
X-rays	·62	·89	·45	·205	0·050
β-rays	·058	·148	·87	6·28	0·047

In concluding this part of the paper, I should like to take the opportunity of thanking Professor S. Russ for supplies of radon, and Mr. J. A. V. Fairbrother for assistance in the experimental part of the work.

§ 5. *Discussion of Results.*

The result arrived at in the last section, that the loss of charge by the colloidal particles is proportional to the energy absorbed in the solution, while not in itself affording us a basis for a theory of the action of ionizing radiations on colloidal solutions, at least enables us to rule out certain possibilities. The absorptions measured in the experiments were absorptions in the sol as a whole, that is mainly in the solvent, since the amount of colloidally-dispersed substance in the sol is too small to affect the absorption much. Now, this will be very different from the absorption of the radiation of the colloid particles. The mass coefficients of X-ray absorption for copper and cerium are about forty times that of water. For beta-radiation, however, the ratio is of the order of two to one. It is clear, then, that for equal absorptions by the sol as a whole the absorption of X-rays by the colloid will be far greater than that of beta-rays, in the ratio, in fact, of nearly twenty to one. The effect on the colloid is, however, practically the same in both cases. Hence the change in the colloid particles must be due to the action of the rays on the solvent, and not a direct action on the colloid particle itself.

Again, the primary effect on the absorption of X-rays is the production of photo-electrons. For an equal absorption of energy the number of these photo-electrons generated will be far greater than the number of beta-particles passing through the solution. We cannot therefore associate the action on the colloid particle with the starting or stopping of a high-speed electron. These considerations seem to show that the "hot spot" theory, which Dessauer has put forward to account for the action of the rays on biological material, are not applicable to colloidal solutions, as a "hot spot" formed in the mass of solvent would hardly retain its high temperature long enough to act on the comparatively large mass of a colloid particle. We are, I think, compelled to look for the cause of the coagulation of the colloids in the one effect which the two types of radiation have in common—the production of ions in the solvent. We have already put forward this suggestion in previous communications. The experiments we have just described provide additional confirmation of our suggestions.

6. *The Action of Ionizing Radiations on Colloidal Solutions.*

There still remains the problem as to whether the discharge of the sol is an immediate effect of the ionization, or whether the ionization brings about some chemical or other change in the medium, which in turn brings about the precipitation of the colloid from solution. Fernau and

Pauli (4) have suggested that the primary effect of the radiation is the production of hydrogen peroxide in the solution, which then coagulates the colloid in the usual way. It is, perhaps, somewhat difficult to disprove this hypothesis, but the following results seem strongly against it :—

(*a*) As has already been reported, exposure of pure water to varying doses of X-radiation does not produce an amount of hydrogen peroxide which is detectable even by the most delicate tests.

(*b*) Experiments recently made in the laboratory show that hydrogen peroxide in dilute aqueous solution is readily decomposed by exposure to X-rays. This result is confirmed by recent experiments of Glocker and Risse (7), who have studied the action quantitatively.

It might, however, be possible to hold that, under the action of the radiation, there is an equilibrium at some very minute percentage, between the water and the hydrogen peroxide, which is maintained by the radiation as the minute traces of hydrogen peroxide present are absorbed by the colloid. To test this somewhat elaborate hypothesis, Bredig solutions of copper were made by sparking between copper rods under ethyl alcohol, and under amyl alcohol. The colloidal copper was precipitated from both these organosols by exposure to X-rays. They were, in fact, decidedly more sensitive to the radiation than the corresponding water sol. It is true that both alcohols would probably contain traces of water, but one would have expected that, with the very small amount of water present, the exposure necessary to produce the amount of hydrogen peroxide required for coagulation would at least have been very much prolonged. Colloidal solutions of silver resinate in oil of lavender and in benzene were also affected by X-rays. Here the amount of water present, if any, must have been very small. On the evidence, then, it seems much more probable that the effect is a direct one, and that the colloidal particles have their charges neutralized by the ions formed in the double layer round them.

There remains the fact, for it seems to be a fact, that only sols in which the particles are positively charged are coagulated either by X- or beta-radiation. Hardy (4), for example, found that positively-charged globulin was coagulated by beta-radiation, but negatively-charged solutions of the same substance were unaffected. Wels and Thiele (8) report the same result, using X-radiation. In the course of the last two years we have examined a large number of sols, with the result that in no case have we been able to coagulate a negatively-charged colloid, and in no case have we failed to produce coagulation where the particles of the sol were positively charged. With sols, such as silver iodide, which can be prepared with the particles either positively or negatively charged, the former are coagulated, the latter are apparently unaffected by the radiation.

It seems to me that the one-sidedness of the effect may be connected with the different nature of the initial positive and negative ions. The positive ion is never smaller than an atom. The negative ion begins as a free electron, and in a gas persists in this state for an appreciable fraction of its existence. Our knowledge of the behaviour of ions and electrons in a liquid medium is very scanty, but it is not improbable that a similar state of affairs exists there also.

We now suppose that the colloid particles are surrounded by a closely adherent film of molecules of the solvent. There is considerable evidence in favour of the view that the surface along which slip takes place when the particle moves under a field is entirely within the solvent and not between the solvent and the particle, and Fairbrother's observation that the size of the colloidal particles decreases as they lose their charge is additional evidence in favour of the supposition. If the colloid is electro-negative it attracts the positive ions formed by the radiation in the double layer surrounding it. The positive ion, however, being molecular, will be unable to penetrate the protecting skin of solvent molecules which surrounds the colloid particle, and remains outside, where it is either neutralized or takes the place of one of the electrolytic ions which form the outer shell of the double layer.

If, however, the particle is electro-positive, so that it attracts the negative ion, the latter, being in an electronic state, and being in an electric field of the order of 10^5 volts per cm., will be able to penetrate the protective skin of solvent molecules and so to neutralize the charge on the particle itself. An alternative suggestion, which experimentally is probably indistinguishable from the first, is that the electron by entering an atom on the outer face of the skin causes the liberation of an electron from an atom on the inner surface in contact with the particle. We have not at present sufficient knowledge to enable us to apply numerical tests to this hypothesis. It seems, however, to be the one which most adequately explains our experimental results on the action of ionizing radiations on colloidal solutions.

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Department of Physics,
University of Reading,
Oct. 27, 1928.

IX. *On the Intensities of some Fe^+ Multiplets in the Arc and Chromosphere Spectra.* By William Clarkson, *Ph.D., M.Sc., International Education Board Fellow, Physical Institute of the University of Utrecht*[*].

Introduction.

RECENT work of Professor Ornstein and T. Bouma (1) on the intensity relations in the multiplet spectra of nickel and cobalt having led to interesting extensions of the multiplet summation rules, the writer undertook, at the suggestion of Professor Ornstein, some intensity measurements on the multiplet spectra of ionized iron. On determining the intensities for the two multiplets selected, $2^4F - 2^4F'$ and $2^4F - 2^4D$ respectively, it was not only possible to compare their variations with the ones predicted by theory, but also to compare them with the ones for the solar emission ("Flash") spectrum, these having been determined during the recent Dutch Eclipse Expedition to Lapland in 1927 (2).

Measurements.

The initial source of spectrum was the middle-fifth of an arc between rods of ordinary iron. The grating used being stigmatic, the convenient step-weakener method of intensity measurements was employed.

To keep ionic concentration, and thus self-reversal, as small as possible it was desirable to use the smallest current practicable. It was found that a current of two amperes could be used, as it gave just the same results as the less convenient minimum of about one-half ampere. That the self-absorption would be expected to be small in both cases was suggested by the very low intensities of the lines.

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[*] Communicated by Professor Ornstein.

Owing to "blending" with nickel and cobalt lines probably having an influence in two critical cases, those of lines 4520 and 4549, the measurements were repeated using poles of electrolytic iron; in this case cobalt was absent and nickel, if indeed present, a mere trace. It was found that, allowance being made for the small effect of these two blends, the results for the two plates were the same.

RESULTS.

The two plates, for ordinary and for electrolytic iron, were photometered several times and the intensities of the lines and of the background were determined. Although analysis of the photograms was necessary in the case of several lines, the results were quite definite.

The background was found to present the one likely source of error. The apparent background, at least, was neither constant, nor did it vary regularly with wave-length. At intervals throughout the plate, however, the background appeared quite line-free and homogeneous, and it was found that for these points the photograms recorded a constant and minimum intensity. Since we cannot allow for the unknown bands or lines which presumably might have introduced blending, and the apparent background had dubious significance, and since in any case local homogeneity would have had to be assumed, the line intensities have been derived, assuming the minimum background to apply throughout the plate. That even in the doubtful cases the error would appear to be negligible is shown by the consistency of the results in comparison with those for the chromosphere.

Table I. tabulates the theoretical intensities with those for the arc and the flash spectra, and with the visual estimations quoted by Russell (3) (for laboratory conditions, but source not given).

Fig. 1 expresses the relation between the theoretical intensities and those for the arc and flash respectively in a graphical form. The log scale is used so that slopes may more readily be compared. The lines joining the points are generally without significance, and are given to stress their general relation and heir erraticity.

Some remarks on the flash results are necessary. In these, two determinations of the intensities, *a* and *b* respectively, using different methods were made. It was found that the application of a conversion factor served to convert *b* into *a* values, and that then the values generally coincided. Some differences, however, were encountered ; in these cases both values are given. The mean has not been given, as the probability is that one of the results is the true one, the other being erroneous. Fig. 3 supports this conclusion and provides the weighted values employed in fig. 1.

TABLE I.

	λ.	Inner Quant. No.	Intensities (units arbit.).			
			Theo.	Flash, *a* & *b*.	Arc.	Russell.
$2^4P - 2^4F$.	4472	3—2	168	28, 20	6	—
	4489	4—3	225	32	10	4
	4491	2—2	472	41, 27	12	4
	4515	3—3	867	46, 51	20	6
	4520	5—4	175	49	66	6
	4534	2—3	168	25 (prob.).	7	—
	4555	4—4	1280	59	24	6
	4582	3—4	225	21	6	—
	4629	5—5	1925	76, 60	25	4
$2^4P - 2^4D$.	4508	2—1	245	42	14	8
	4522	3—2	392	64	25	6
	4541	2—2	98	27, 24	7	—
	4549	4—3	600	? 50 ?	60	4
	4576	3—3	128	25, 22	8	4
	4583	5—4	875	80, 102	28	8
	4620	4—4	100	19	5	—

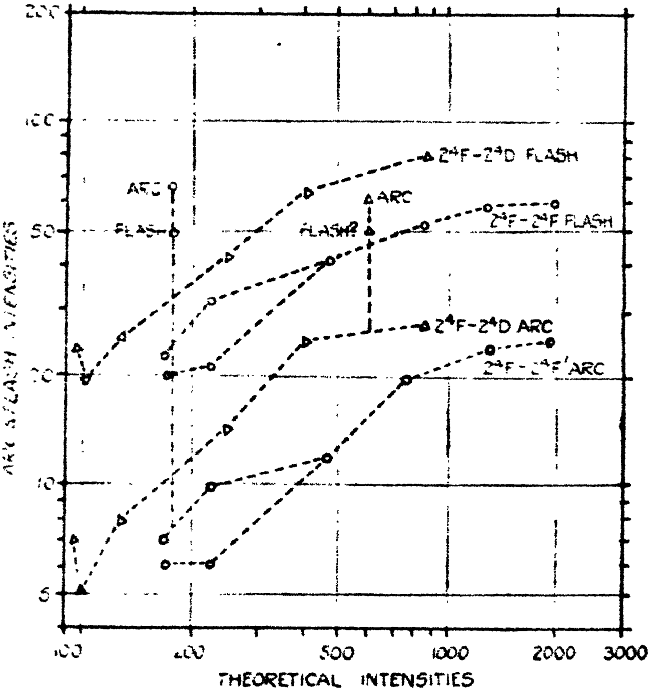
The flash intensity of the line 4549 remains doubtful, as its intensity cannot be freed from the effects of blending with the much more intense Ti^+ line. It can be awarded a minimum intensity of about 40, and since the peaks of the lines do not coincide, probably of about 50 (the value used here); but the purely speculative nature of these, and the fact that there must be abnormal self-reversal due to the influence of the titanium, prevents quantitative comparisons with the corresponding arc line being possible.

DISCUSSION.

1. *Comparison with Theoretical Multiplet Rules.*

It will be seen (fig. 1) that there is a close general resemblance between the curves for the same multiplet, but that however these measured values for the arc and flash agree among themselves, they show little correlation with the theoretical intensities. This disparity is exhibited most markedly in the case of one line in each multiplet. The first line, 4520, is also highly abnormal in the flash spectrum, though not to such a great extent as in the arc; unfortunately the second, 4549, is the line of doubtful intensity. It is interesting that the value allotted it makes it abnormal in

Fig. 1.



the flash in a reverse direction; but one cannot build on this, as it might easily be the result of the abnormal self-reversal previously mentioned.

That there are well-established, if at present little understood, causes of deviation inherently present in complex electronic systems immediately suggests the explanation of those found here, should it be found that they are not due to such a factor as self-reversal.

For this we may compare the results in two ways:—(*a*) The arc and flash results with the multiplet summation rules, particularly those recently established for the equally complex cases of nickel and cobalt (this will check the results from a theoretical standpoint ⁽¹⁾); and (*b*) the arc results with the emission ("flash") spectrum of the chromosphere (here there should be no effect due to abnormal conditions of excitation, and certainly an effect due to self-absorption ⁽²⁾).

TABLE II.

		$2^4F'$.				2^4D.				Summations.		
		2	3	4	5	1	2	3	4	Theo.	Arc.	Flash
2^4F.	2	12	7			14	9	×		990	$^{19}40^{21}$	132
	3	6	20	6			25	8	×	1785	$^{32}65^{33}$	181
	4		10	24	?6			60	5	2380	$^{40}105^{65}$	183
	5			66	25				28	2975	$^{91}119^{29}$	189

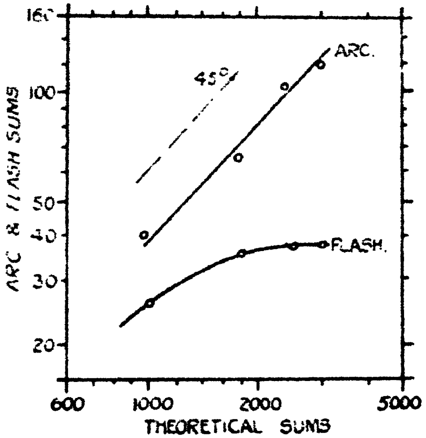
2. *Comparison with Theoretical Summation Rules.*

Table II. presents the intensity scheme for the arc, with total summations for the theoretical intensities and for the arc and flash. On the one hand the sums of the individual multiplets are found to exhibit no correlation with those predicted, on the other the total sums will be seen to be in excellent accord.

Intensity measurements have previously revealed that in several cases, though the theory did not meet the case of the individual lines, it agreed with the sums quite well. More recently(1) it has been shown, from the cases of nickel and cobalt, that even this might not apply, but that again an extension of the rules, this time to the total sums of each system of two or four multiplets, brought about correspondence. Table II. shows that the multiplet spectrum of ionized iron must be included under this category.

How close this linear relation is, the lines of "abnormal" intensity notwithstanding, is well shown in fig. 2. Indeed, with respect to the two normal lines, we see that it is only their great virtual irregularity which caused the close correspondence between the total sums to be preserved.

Fig. 2.



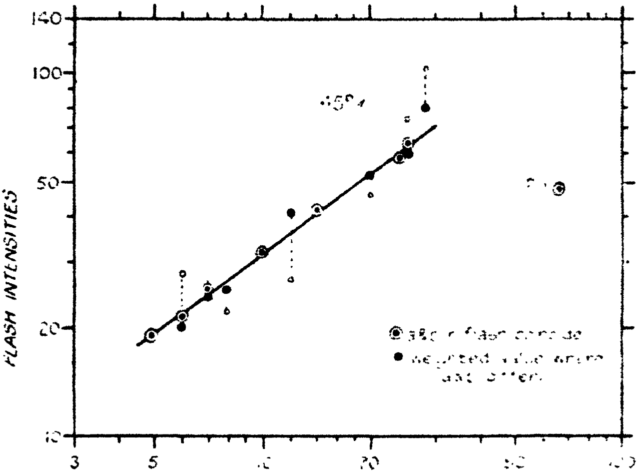
The results for the flash, which show corresponding individual variations to those for the arc, are equally illuminating, for even though here the total sums do not correspond to the theoretical ones at all, yet their curve also is continuous, thus showing that a close correlation exists. Indeed, we should expect a curve of this form to show the expected self-reversal of the solar spectrum, whilst the 45° slope of the arc curve justifies our opinion that self-absorption is inappreciable in its case. The total sums thus give the insight into the true phenomena apparently denied by the individual results.

3. *Arc-Flash Comparison.*

Should the deviation of measures from theoretical values in the case of the intensities of individual lines be due, as suggested, to the inadequacy of the theory, and should the arc be free from self-absorption, we may accept the intensity values for the latter as the legitimate supplanters of the theoretical ones. In this case, since self-reversal would appear to be the only additional factor operating to modify the chromospheric intensities, the arc and flash spectra should show a correlation extending to the individual lines.

Fig. 3 shows the relations between arc and flash values. The incontrovertible points lie on a straight line, with slope less than 45°, and of the doubtful points the suggestion that one of each pair would probably be valid appears to have

Fig. 3.



been warranted. This result is most satisfactory. In connexion with the form of the graph, it is instructive to note that when all the points for the series of ionized iron multiplets are plotted against the theoretical values a similar straight line (though of somewhat different slope) is found to apply.

There is, however, one serious divergence from this relation, and this is of a disturbing nature ; the two lines of particularly abnormal intensity, 4520 and 4549, give points lying a long way off the curve. In attempting an explanation, all we can scrutinize is the validity and significance of the flash intensities, for in view of the evidence we must assume that the lines actually do belong to the multiplets, and the arc values may be taken as basis.

There can hardly be errors of an observational nature, and blending would serve but to exaggerate the divergence ; yet to fit the points to a linear relation would demand the increasing of the observed intensities of 50–60 to about 120–30 ; fitting them to the maximum curve possible would only reduce this to 90 or so. It is not impossible that these lines, having abnormal intensity, may also be subject to abnormal self-reversal ; but though this is a quite plausible assumption, the data available do not permit us to proceed so far with correction. In the circumstances the problem of these lines must be left as presented, as an experimental fact.

The writer is greatly indebted to Professor Ornstein, at whose instigation this problem was taken up, and to Dr. Minnaert, of the Heliophysical Department, for the furtherance of this research, and to the International Education Board for the Fellowship, during the tenure of which this work was carried out.

Summary.

Results of intensity measurements of the multiplets $2^4F-2F'$ and 2^4F-2^4D for ionized iron, for an iron arc, and for the chromosphere ("flash" spectrum) are treated. Both show similar wide divergencies from theoretical intensities of individual lines ; one line in each multiplet is particularly "abnormal."

Comparisons of multiplet summations show :—

(*a*) In ionized iron, as in nickel and cobalt, the multiplet summation rules only apply when extended to the total sums of the two multiplets (Ornstein and Bouma).

(*b*) The arc is free from self-absorption, and thus gives the fundamental line intensities. The flash sums demonstrate self-absorption.

The flash-arc relation is linear, but the two very abnormal lines lie off this curve. This is briefly discussed.

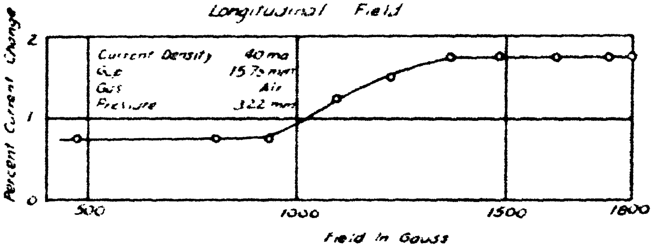
References.

(1) Ornstein & Bouma (pending).
(2) Pannekoek & Minnaert, *Kon. Akad., Amsterdam,* part 13, no. 5 (1928).
(3) Russell, Ap. J. lxi. p. 223 (1925).

X. *Control of Current in a Discharge-Tube by Means of a Magnetic Field.—By* ROBERT F. EARHART *and* CHARLES B. GREEN [*].

IN certain experiments involving the discharge of electricity through gases, moderately high potentials are required to produce and maintain a discharge. Control of current through the circuit is usually effected by variable resistances in the circuit. On page 481 of 'Conduction of Electricity through Gases,' Sir J. J. Thomson describes an experiment in which it was desired to alter the current in the circuit without varying the impressed e.m.f. or disturbing the ordinary constants of the circuit. For this purpose a Wehnelt cathode was used in a spark gap and this was placed in a longitudinal magnetic field. Variation in the current passing through the circuit was produced by altering the field. This has the effect of introducing a "valve" into the circuit, one which may be regulated by a control outside of the circuit proper.

Fig. 1.



One of us [†] had previously made some experiments on the effect of applying a magnetic field across a discharge gap under a limited range of conditions. In connexion with some extensions of the experiments, we have been led to study the extent of such valve control and the optimum conditions for applying it. Instead of using a Wehnelt cathode, a discharge was produced between plane, parallel, brass plates at ordinary temperatures. It was found that, if the distance between such electrodes was several cms., an increase in the current was produced upon applying a longitudinal field, but that this effect was small, especially for a current of several milliamperes. It was found further that if the distance between the plates was reduced to the order of 1 mm. and the pressure properly adjusted, variations in current produced by varying the field might be as much as several hundred per cent. Figs. 1 and 2 indicate the extent of such a change.

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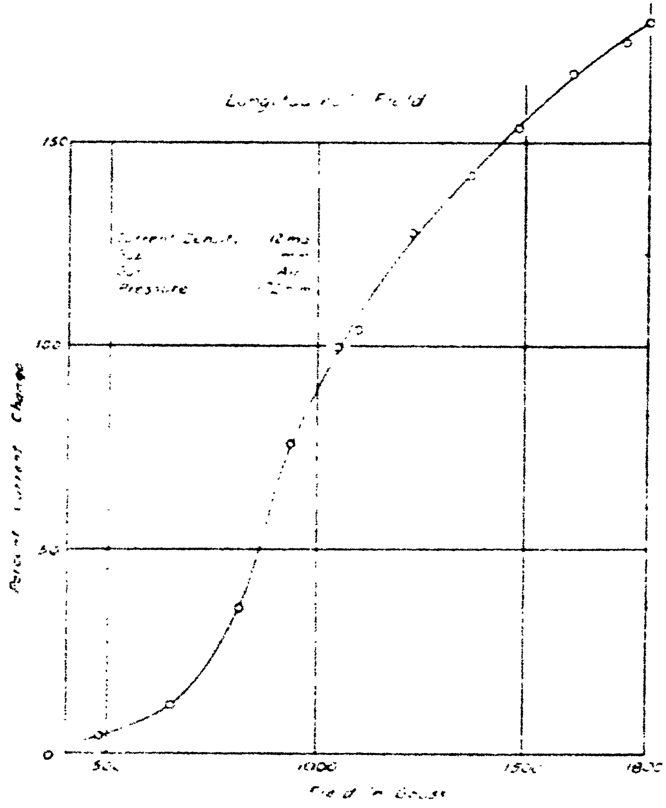
[*] Communicated by the Authors.

[†] Robt. F. Earhart, 'Physical Review,' Aug. 1914.

Attention is called to the difference in scale used to show the percentage change.

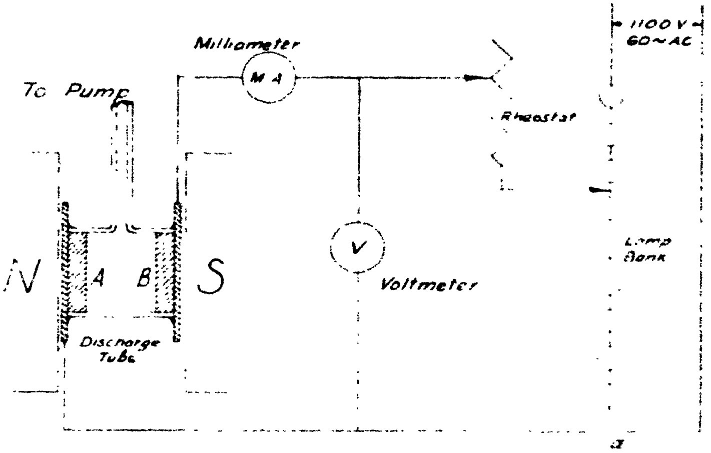
Fig. 2.



The accepted explanation for the increase in current under the influence of such a field, is that increase in ionization by collision occurs due to the helical motion of such ions as initially have a velocity component perpendicular to the electric force. Possibly this might give rise to another effect which would limit or even cause a decrease in the current, viz., that the ions which execute such motion might spiral out of the path between the electrodes and be dispersed to the sides of the supporting tube. Our experiments can be interpreted if both effects exist.

A. W. Hull[*] published a paper in which a study was made of similar effects. A part of his paper dealt with a radial discharge of electrons produced from an incandescent wire to an outer co-axial cylindrical electrode and with a magnetic field applied parallel to the axis of the tube, thus giving a transverse field. The experiment was made in high vacuo so that it could be assumed that the mean free path of the electron was greater than the distance between the electrodes. This type of problem is amenable to calculation, and he found good agreement between the computed distribution of electron current and the measured values. The experimental conditions of our experiment preclude simplifying assumptions either as to mean free path or for unsaturated currents. Ions formed in air are complex in character, and in no case was the mean free path small compared with distance between electrodes; moreover, if increase in ionization is caused by increase in path due to the helical motion of an ion, then, when a collision occurs, the new ions thus formed would tend to execute a spiral motion starting from the point at which they originate.

Fig. 3.



The possible results are not amenable to calculation by any methods with which the authors are familiar.

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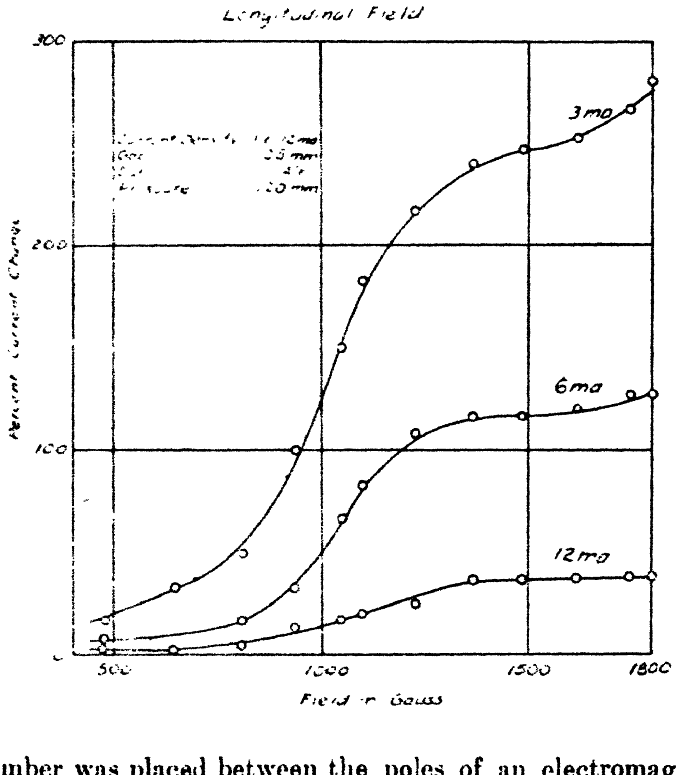
[*] A. W. Hull, 'Physical Review,' July 1921.

Fig. 3 indicates the arrangement of the apparatus used. A transformer stepped up 60-cycle A.C. current to 1100 volts which was sent through 12 lamp filaments in series. By tapping off from these and introducing a liquid rheostat, suitable e.m.f.'s could be applied to the electrodes A and B placed in a discharge chamber and the initial currents regulated. The electrodes were cut from a brass rod 1·8 cm. in diameter and fitted closely in a glass tube. The discharge chamber was placed between the poles of an electromagnet provided with large flat pole-pieces. The magnetic field was calibrated and explored by means of a flip coil in the usual manner.

Fig. 4.

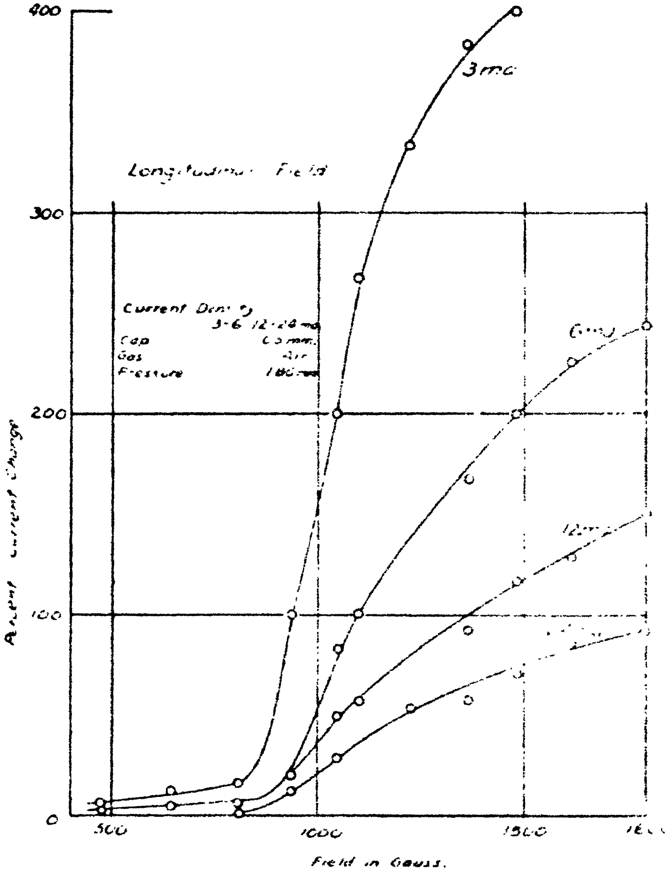


It was soon found that variation in the current effected by altering the magnetic field depended on the magnitude of the current passing across the gap. A failure to recognize this as one of the variables is possibly responsible for lack of agreement between results reported by different observers.

There appear to be at least three variables which will modify the changes produced by application of the field :—

(1) Distance between electrodes.
(2) Pressure of gas in the chamber.
(3) Magnitude of the current under stress.

Fig. 5.



Figs. 4 to 6 inclusive show the character of changes produced when the distance between the electrodes is small.

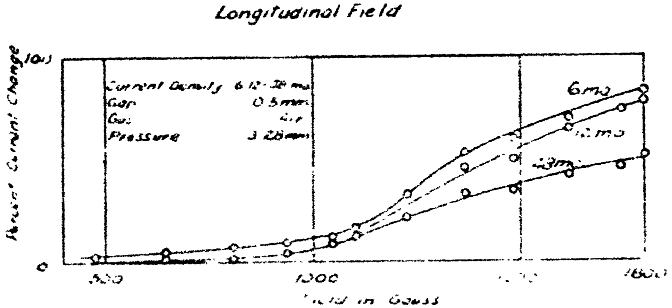
Referring to fig. 4, it appears that the larger currents, *i. e.*, those of 6 and 12 milliamperes, are less changed by the field than the 3 milliampere current. Indeed, for larger currents rather moderate fields produce a condition such that further increase in field strength does not add much to the change. This relation appears in each of the families of curves in figs. 5 and 6. This "saturation effect" applies equally well to the smallest current which we have used but for higher values of the magnetic field than shown in the graphs.

Fig. 6 indicates the extent to which control is reduced with increase in pressure. The general inference is that the maximum control by the longitudinal field is obtained for small currents, through small distances, and at a pressure near the critical pressure.

Experiments with hydrogen afforded families of curves of the same type as those for air.

A series of experiments was made with one electrode a point, the other a plane. It is well-known that for pressures of the order used, ·5 mm. to 5 mm., there is a large factor of rectification of an A.C. current. This rectified current was measured by adding a D.C. milliameter to the circuit. The unidirectional current was affected by the magnetic field in much the same way as the sinusoidal current. Graphs for this are omitted.

Fig. 6.



Experiments with Transverse Fields.

It is generally assumed that the application of a transverse magnetic field will diminish the current flow across a discharge gap and ultimately extinguish it, if the field intensity is sufficiently great. Indeed, the magnetic blow-out of an arc is a well-known application of this phenomenon.

Our experiments show this to be the case if the distance between the electrodes is large (5 cm.), or the pressure exceeds a few mm. J. E. Ives* noted an exception to this commonly observed fact. He found that a current of 1 milliampere which passed between electrodes under a pressure of ·18 mm. was increased by a transverse magnetic field. Our experiments confirm Ives' experiment. Especially is this the case when the distance between the electrodes is small. The helical motion of an ion spiraling along a line of magnetic force would increase ionization by collision, and this might be quite effective in augmenting the current, especially if the area of the electrodes was large compared with the distance separating them.

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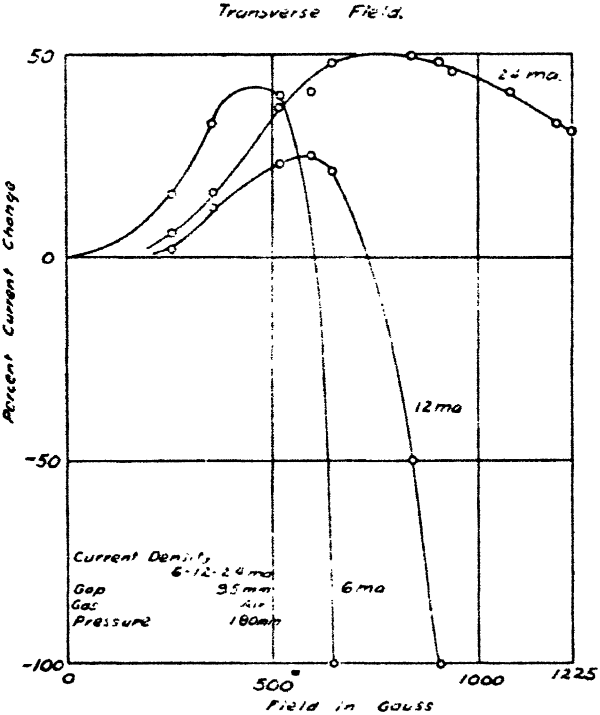
* J. E. Ives, 'Physical Review,' Oct. 1918.

Fig. 7.



We have found that, for small distances and pressure properly adjusted, fields of a few hundred gauss may considerably increase the current, while larger fields may reduce the current. Current density again appears as a variable, as was the case with longitudinal fields. This effect is represented graphically in fig. 7.

Fig. 8 indicates the part that pressure plays in these variations. The initial current, *i.e.* with zero field, was 24 m.a. in each case. This shows that the percentage change produced by field is diminished with increase in pressure. In fig. 9 the extent to which changes in length of gap affect the variation is shown.

In one of our experiments the electrodes were separated 5 cm. and a uniform glow produced in the tube with the field off. The axis of the tube was horizontal, likewise the lines of magnetic force were horizontal and perpendicular to the electric force. Upon applying a small field, the discharge was broken up into transverse striæ which appeared at the top and bottom of the tube, while the core and sides were free from luminous striations ; this might be expected by applying the Fleming left-hand rule. As the field strength was varied, the striations could be made to

Fig. 8.

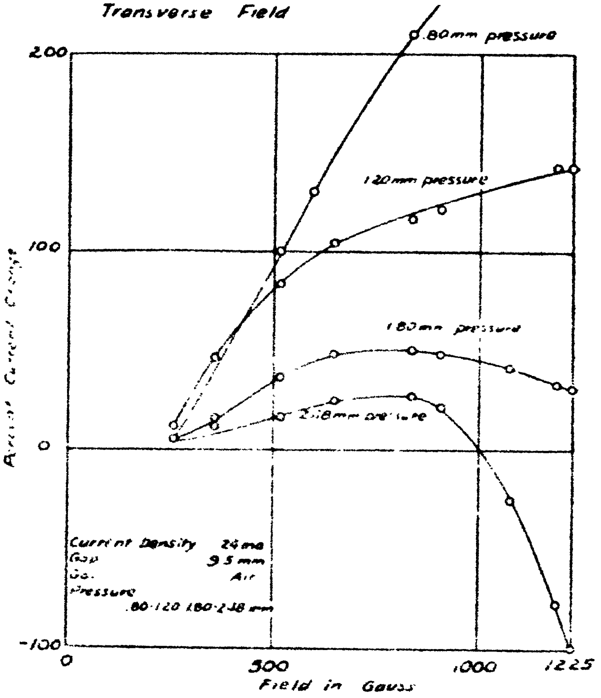


Fig. 9.

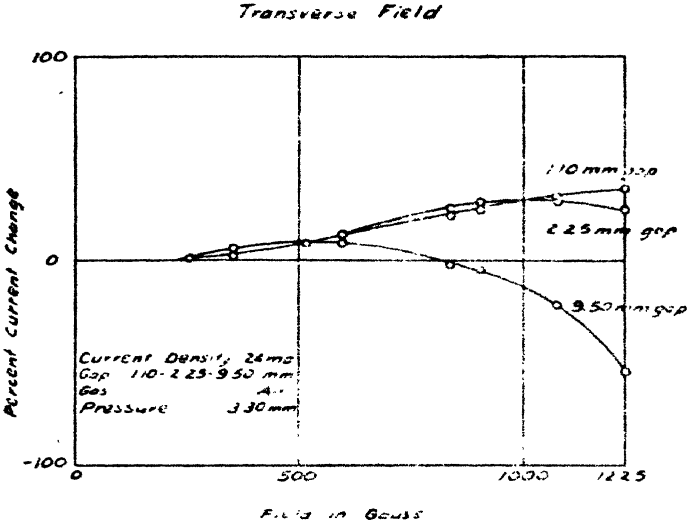
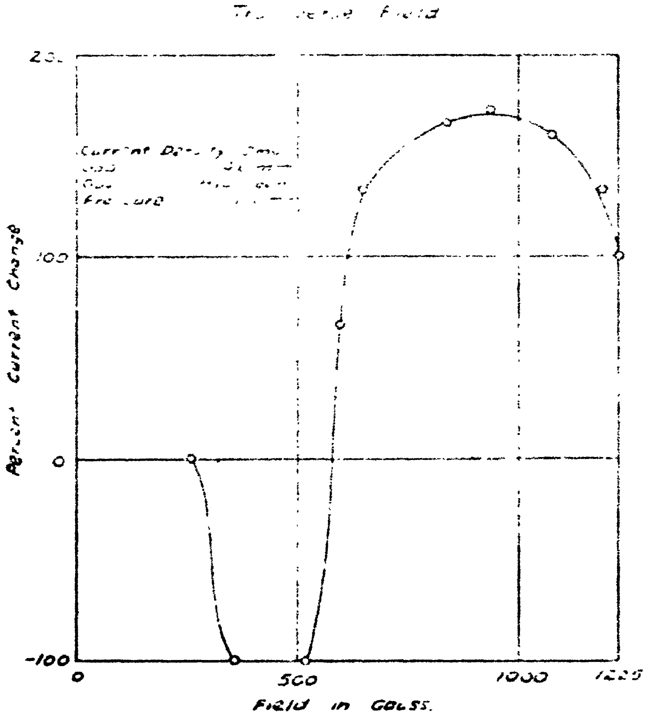

Transverse Field
100
0
-100
Percent Current Change
0
500
1000
1225
Field in Gauss
110 mm gap
2.25 mm gap
9.50 mm gap
Current Density 24 ma
Gap 110-2.25-9.50 mm
Gas A
Pressure 3.30 mm

Fig. 10.


Transverse Field
200
100
0
-100
Percent Current Change
Current Density
Gap
Gas
Pressure
0
500
1000
1225
Field in Gauss.

progress back and forth, but with increase in field were crowded against the walls of the tube until extinction occurred.

There is a critical region of pressure and distance where the form of these graphs alters. In some experiments with hydrogen, it was found that a magnetic control could be effected where small fields would decrease the current quite uniformly to 50 or 60 per cent. of the original value, while larger fields restored and even increased the current by more than 100 per cent. (fig. 10) shows an extreme case where the application of a transverse field of from 300 to 500 gauss extinguished the discharge, while slightly higher fields restored it, and an application of 1000 gauss more than doubled the current. The application of still higher fields reduced the current finally to the point of extinction and here the extinction was final.

Mendenhall Physical Laboratory,
Ohio State University, U.S.A.,
June 1928.

XI. *On the Condenser-Telephone.* *By* G. Green, *D.Sc., Lecturer in Physics in the Applied Physics Department of the University of Glasgow* *.

In a former paper under the above title which appeared in the Phil. Mag., Sept. 1926, pp. 497–508, a preliminary discussion is given of the mathematical theory of the condenser-telephone. The discussion there given is, however, limited to a special case, namely, that of a condenser consisting of two plates only separated by a dielectric sheet of elastic material, one of the plates being regarded as fixed and the other as free to move in response to electrical vibrations transmitted to the condenser circuit. The condenser circuit is understood to consist of a transformer secondary coil of inductance L and a battery of e.m.f. E in series with the condenser, the total resistance of the circuit being R ; and the problem considered in the earlier paper is to determine the motion of the free plate of the condenser when a small periodic e.m.f., $e \sin \omega t$, is applied to the circuit by means of the transformer. For certain purposes the two-plate condenser-telephone is worthy of study, but the case of a condenser consisting of a pile of plates of which one only, the undermost plate, is regarded as fixed, while all the others are free to move in response to electrical vibrations, is more important, as condensers of this type are likely to find more general application. The investigation of the more general case is interesting in itself, and is desirable for the satisfactory understanding of the dynamical theory of the condenser-telephone.

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* Communicated by the Author.

Consider a condenser consisting of parallel plates numbered 0, 1, 2, 3, ..., n respectively. Take plate number 0 as fixed in position in a vertical plane, while the other plates are at successive distances d, $2d$, $3d$, etc., from it, each plate being just in contact with the dielectric material which separates the plates, but not exerting any more force upon it, when the condenser is uncharged. For our purpose it is convenient to regard this whole condenser as made up of n separate condensers arranged in parallel, plates 0 and 1 forming condenser No. 1, plates 1 and 2 forming condenser No. 2, and so on up to No. n. When the separate condensers are charged each with charge Q_0 electromagnetic units, the plates are alternately positive and negative, and the uniform distance between each pair of consecutive plates is altered from d to $(d-a)$, where a is given by the equation

$$\mathrm{YA}\frac{a}{d}=\frac{2\pi Q_0^2 r^2}{\mathrm{A}k}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the notation employed being the same as that of the earlier paper, with Y as the Young's Modulus of the dielectric material. This equation defines the equilibrium position of the plates when each constituent condenser has the charge Q_0. The uniform charge Q_0 on each side of each plate may also be looked upon as due to the constant e.m.f. E acting between the plates. When a variable e.m.f., $e \sin \omega t$, is superposed upon the steady e.m.f. E acting in the circuit, the coordinates defining the positions and charges on the plates at any instant t can be chosen with reference to the equilibrium condition of the system. Thus we may take $x_1, x_2, x_3, \ldots, x_n$ to denote the displacements of the plates from their equilibrium positions towards the fixed plate at instant t, and Q_0+q_1, Q_0+q_2, Q_0+q_3, ..., Q_0+q_n, to denote the charges on each of the successive condensers. The sum of all the charges on all the positive plates, or on all the negative plates, is thus $nQ_0+\Sigma q$ at instant t.

We can now write down the equations of motion of the plates. The forces acting on each plate of the condenser consist of the mutual electrostatic attractions between the plate and the two plates immediately in its front and rear respectively, together with the pressure forces applied to it by the dielectric material in contact with it on either side. Thus the equation of motion of any one of the plates, with the exception of the outermost plate, which communicates its motion to the air on its open side, is indicated completely by an equation of the type shown for plate r below :—

$$m\ddot{x}_r = \frac{2\pi v^2}{Ak}\{(Q_0+q_r)^2-(Q_0+q_{r+1})^2\}$$
$$-YA\frac{a+x_r-x_{r-1}}{d}+YA\frac{a+x_{r+1}-x_r}{d}. \quad . \quad (2)$$

Here the mass m must be taken to represent the sum of the masses of the metallic plate and of the sheet of dielectric material in contact with it on one side. In the case of the outermost plate, the reaction of the air on the open side can be represented by a resistance term proportional to the velocity $\kappa\dot{x}_n$, as we have found in the earlier investigation. Hence the equation of motion of the outermost plate becomes

$$m\ddot{x}_n = \frac{2\pi v^2}{Ak}(Q_0+q_n)^2-\kappa\dot{x}_n-YA\frac{a+x_n-x_{n-1}}{d}. \quad . \quad (3)$$

Before we can obtain the solution of these equations, the quantities $q_1, q_2, q_3, \ldots, q_n$ must first be expressed in terms of $x_1, x_2, x_3, \ldots, x_n$, the displacements of the plates. This can be done by making use of the equation to the condenser circuit itself and of certain relations which hold between the separate parallel condensers composing the complete condenser at any instant.

According to the notation employed in the former paper, if we denote by C_0 the capacity of any one of the condensers in parallel when all the plates occupy their equilibrium positions, and by C_r, the capacity of condenser r at instant t, we find that

$$C_r = C_0\left[1+\frac{x_r-x_{r-1}}{d-a}\right], \quad . \quad . \quad . \quad . \quad (4)$$

first-order terms only being retained; and also that the capacity of the complete condenser is represented by

$$\Sigma C = nC_0\left[1+\frac{x_n}{n(d-a)}\right]. \quad . \quad . \quad . \quad . \quad (5)$$

If we let $Q = nQ_0 + \Sigma q$ represent the total charge upon the condenser at any instant, the equation to the condenser circuit may be written in the form

$$L\frac{d^2Q}{dt^2}+R\frac{dQ}{dt}+\frac{Q}{\Sigma C}=E+e\sin\omega t; \quad . \quad . \quad (6)$$

and in view of the relation $nQ=E\Sigma C$ and of (5) above, the equation to the circuit becomes, finally,

$$L\frac{d^2\Sigma q}{dt^2}+R\frac{d\Sigma q}{dt}+\frac{\Sigma q}{nC_0}=e\sin\omega t+E\frac{x_n}{n(d-a)}. \quad . \quad (7)$$

In this case we may assume that x_n can be represented by $X\sin(\omega t+\epsilon)$, and the solution can immediately be written down as in equations (6), (7), and (8) of the previous paper, referred to above. We have, accordingly,

$$\Sigma q=\alpha\left\{e\sin\omega t+E\frac{x_n}{n(d-a)}\right\}-\beta\left\{e\cos\omega t+E\frac{x^n}{\omega n(d-a)}\right\},$$

where

$$\alpha=\frac{nC_0(1-nC_0L\omega^2)}{D^2}=\frac{nC_0\cos\theta}{D},$$

$$\beta=\frac{Rn^2C_0^2\omega}{D^2}=\frac{nC_0\sin\theta}{D}.$$

and

$$\tan\theta=\frac{RnC_0\omega}{(1-nC_0L\omega^2)}, \text{ and } D^2=\{(1-nC_0L\omega^2)^2+R^2n^2C_0^2\omega^2\}. \quad . \quad . \quad . \quad (8)$$

The additional relations which we require in order to eliminate the oscillatory charges $q_1, q_2, q_3, \ldots, q_n$, from equations (2) and (3), above are obtained from the condition that at any instant each of the separate condensers in parallel of which the complete condenser is composed, has the same potential difference $E+e\sin\omega t$ between its plates. We thus obtain the equations

$$\frac{Q_0+q_1}{C_1}=\frac{Q_0+q_2}{C_2}=\ldots=\frac{Q_0+q_r}{C_r}=\ldots\frac{nQ_0+\Sigma q}{\Sigma C}, \quad (9)$$

and as each of the terms appearing in this can be expanded as follows:

$$\frac{Q_0+q_r}{C_r}=\frac{Q_0}{C_0}\left[1-\frac{x_r-x_{r-1}}{d-a}\right]+\frac{q_r}{C_0}, \quad . \quad . \quad (10)$$

we find, finally, that

$$q_r-q_{r-1}=\frac{EC_0}{d-a}(2x_r-x_{r-1}-x_{r+1}). \quad . \quad . \quad (11)$$

For the present, in order to take the simplest case for mathematical analysis, we are assuming that all the quantities $q_1, q_2, q_3, \ldots q_n$ are small compared with Q_0, and that their squares are negligible in equations (2) and (3). These equations, by means of the results contained in (8) and (11) above, we can now write in terms of $x_1, x_2, x_3, \ldots, x_n$, and their derivatives. Instead of (2) we now have

$$\left.\begin{array}{l} \ddot{x}_1 = -c^2(2x_1 - x_0 - x_2) : \quad \text{with } x_0 = 0 \\ \ddot{x}_r = -c^2(2x_r - x_{r-1} - x_{r+1}) \end{array}\right\} \quad . \quad . \quad (12)$$

for all values of r up to $n-1$, and

$$c^2 = \frac{\text{YA}}{md} - \frac{\text{E}^2\text{C}_0}{m(d-a)^2}.$$

Instead of (3) the equation to the outermost plate may now be written in the simpler form :

$$\ddot{x}_n = -2\text{K}\dot{x}_n - c^2(x_n - x_{n-1}) - \text{A}'x_n + \text{B}\sin(\omega t - \theta); \quad (13)$$

where

$$2\text{K} = \left[\frac{\kappa}{m} + \frac{\text{E}^2\text{C}_0 \sin\theta}{mn\omega(d-a)^2\text{D}}\right],$$

$$\text{A}' = \frac{\text{E}^2\text{C}_0}{mn(d-a)^2}\left[1 - \frac{\cos\theta}{\text{D}}\right],$$

$$\text{B} = \frac{e\text{EC}_0}{m(d-a)\text{D}}.$$

The complete solution of the system of equations contained in (12) and (13) above can be obtained by well-known methods [*], but, even without this, important information regarding the dynamical theory of the condenser-telephone can be derived from the equations as they stand. The above equations are, in fact, similar to those representing the disturbed motion of a series of masses, each mass being suspended from the mass preceding it in the series by a vertical spring, and the uppermost mass being similarly suspended from a fixed support To let this system correspond exactly with the condenser-telephone system described above, we have merely to suppose that the masses are all equal and that the springs are also all equal, and that the lowest or nth mass is operated on by forces represented by the K, A′, B terms shown in equation (13) in addition to the force applied to it by the spring connecting it to the mass above it. These forces evidently consist of a frictional resistance proportional to the velocity, a restoring force proportional to the displacement, and a disturbing periodic force. The motion of the condenser plates is therefore to be identified with that of a dynamical system whose general characteristics have been fully investigated elsewhere [†].

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[*] See, for instance, Rayleigh, 'Theory of Sound,' vol. i. chap. v.

[†] Lord Kelvin's 'Baltimore Lectures.'

For our particular purpose it is desirable first to form an estimate of the relative importance of the various terms appearing in the equations, such as the fundamental constant c^2 and the damping coefficient K. Probably the minimum value obtainable for the modulus Y would be that which corresponds with air as the dielectric material between the plates, namely, 1·42 × 10^6 dynes per sq. cm. Taking A the area of each sheet as 6 sq. ft. or 5400 sq. cm., and d or $d-a$ as $\frac{2}{1000}$ inch or ·005 cm., and E as 200 volts, the values obtained are

$$\frac{\mathrm{YA}}{d} = 1{\cdot}4 \times 10^{12} \text{ dynes per cm.}:$$

$$\frac{\mathrm{E}^2\mathrm{C}_0}{d^2} = 3 \times 10^9 \text{ dynes per cm.}$$

As we have chosen a minimum value for Y in forming this estimate, it appears that with any solid material as dielectric we may take $c^2 \doteqdot \mathrm{YA}/md$, even with E = 500 volts; and we may consider that the term containing A′ in equation (13) is small enough to be practically negligible in comparison with the terms retained, especially when n, the number of sheets, is any fairly large number. On page 504 of the earlier paper it is shown that the coefficient κ, which appears in the expression for K given in (13), has the value $\mathrm{A}\rho_0\mathrm{V}$, where ρ_0 represents the density of air, and V represents the velocity of sound in air. Taking the same value for A as before, we obtain as the value of κ, 2·27 × 10^5. The remaining term in the expression for K can be estimated from the value just given for $\frac{\mathrm{E}^2\mathrm{C}_0}{(d-a)^2}$. From this it appears that K also is a small quantity compared with c^2. The resistance coefficient, moreover, has its maximum value near the frequency corresponding to electrical resonance and falls off rapidly to the steady value $\frac{\kappa}{2m}$ at the higher frequencies.

The motion of any one of the condenser plates represented by equations (12) and (13) above is evidently of the type

$$x_r = a_r \sin(\omega t - \theta - \epsilon_r),$$

where a_r and ϵ_r are constants. In this case the quantity with which we are specially concerned is the amplitude of the displacement of the outermost plate of the system which transmits sound energy to the air. For a condenser consisting of two plates, the amplitude is given by

$$a_1 = \mathrm{B} \cdot \frac{1}{\sqrt{\{(c^2-\omega^2)^2+4\mathrm{K}^2\omega\}}} \quad . \quad . \quad . \quad . \quad (14)$$

For a condenser having three plates, $n=2$, the amplitude is given by

$$a_2 = \mathrm{B} \cdot \frac{(2c^2-\omega^2)}{\sqrt{\{(\omega^4-3c^2\omega^2+c^4)^2+4\mathrm{K}^2\omega^2(2c^2-\omega^2)^2\}}} . \quad (15)$$

For $n=3$, we have

$$a_3 = \mathrm{B} \cdot \frac{(\omega^4-4c^2\omega^2+3c^4)}{\sqrt{\{(\omega^6-5c^2\omega^4+6c^4\omega^2-c^6)^2+4\mathrm{K}^2\omega^2(\omega^4-4c^2\omega^2+3c^4)^2\}}}, \quad . \quad . \quad . \quad (16)$$

and for the case of n free plates, we have

$$a_n = \mathrm{B} \cdot \frac{f(n, c, \omega)}{\sqrt{\{\mathrm{F}(n, c, \omega)\}^2+4\mathrm{K}^2\omega^2\{f(n, c, \omega)\}^2}}, \quad (17)$$

where $\mathrm{F}(n, c, \omega)$ and $2\mathrm{K}\omega f(n, c, \omega)$ are the real and imaginary parts respectively of the determinant, ∇, obtained by eliminating all the variables but one from the equations of motion, and indicated below for the case of $n=4$:

$$\nabla = \begin{vmatrix} \mathrm{D}^2+2c^2, & -c^2 , & & \\ -c^2 , & \mathrm{D}^2+2c^2, & -c^2 , & \\ & -c^2 , & \mathrm{D}^2+2c^2, & -c^2 , \\ & & -c^2 , & \mathrm{D}^2+2\mathrm{KD}+c^2. \end{vmatrix} . \quad (18)$$

In this the operator D is to be replaced by $i\omega$: and the A' term is omitted as its effect on what follows is very small.

Equation (14), it will be seen, is in agreement with the corresponding result contained in equation (11) of the previous paper. In all cases the amplitude of the displacement of the outermost plate depends on the product of two factors, one being the amplitude of the forced vibration $\frac{e\mathrm{EC}_0}{m(d-a)\mathrm{D}}$ and the other, which we may denote by $\mathrm{F}(n)$, being a function whose value is determined by the elastic modulus of the dielectric material and by the number of sheets contained in the condenser. Neither factor becomes zero as the frequency of the forced vibration $\omega/2\pi$ tends to zero. When $\omega=0$, the value of the amplitude is given by

$$a_n=\frac{e\mathrm{EC}_0}{m(d-a)}\cdot\frac{n}{c^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

from which it appears that the amplitude at low frequencies increases directly as the number of sheets in the condenser.

The curve representing the amplitude of the nth plate for all values of the frequency, $\frac{\omega}{2\pi}$, has always one maximum or resonance point determined by the values of L, $n\mathrm{C}_0$, R, in the condenser circuit. This maximum occurs at the frequency $\frac{\omega}{2\pi}=\frac{1}{2\pi\sqrt{n\mathrm{C}_0\mathrm{L}}}$, and it is possible to choose conditions in the condenser circuit so as to make the amplitude curve either sharp or exceedingly flat in the neighbourhood of this maximum. This is illustrated by three curves representing the variation of $\frac{n\mathrm{C}_0}{\mathrm{D}}$ over the frequency range 0–1000, given in the earlier investigation, p. 506. In the case of a condenser having one free sheet only, a second maximum appears on the curve at the frequency corresponding to $\omega^2=c^2$, which we shall refer to as the standard mechanical frequency of the condenser. If the dielectric material be air, and if ·005 gram per sq. cm. be taken as a value of $\frac{m}{\mathrm{A}}$ for tinfoil sheets, and if d, the distance apart of the condenser sheets, be taken as one mil, the value of the standard mechanical frequency works out at about 50,000. From some results obtained for condensers with paper dielectric the value of the standard mechanical frequency in that case appears to be also in the neighbourhood of 50,000, which seems to indicate that the elastic resistance to compression of the dielectric is largely due to that of the air included between the plates. In the case of a condenser having n free sheets, the amplitude curve has n maxima in addition to the maximum corresponding to resonance in the condenser circuit. These maxima occur at frequencies given approximately by the values of ω determined by the roots of

$$\mathrm{F}(n, c, \omega)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

In (17) these roots determine the frequencies of the free vibrations of the system under the supposition that the frictional resistance term is negligible. The effect of the resistance term is, in general, to reduce the values of the frequencies of the free vibrations slightly below those given by (20), and, as our treatment is approximate, we may consider the values given by (20) as sufficiently near the true values for our purpose. The problem of determining the roots of equation (20) is one which has been solved in connexion with the analogous dynamical system of masses and springs referred to above (see Routh, 'Dynamics of a Particle,' § 305, p. 193). From this we obtain the result that the values of the frequencies corresponding to the free vibrations of the n plate condenser are given by

$$\frac{\omega_s}{2\pi}=\frac{c}{2\pi}\cdot 2\sin\frac{2s+1}{2n+1}\cdot\frac{\pi}{2}, \quad . \quad . \quad . \quad . \quad (21)$$

where s may have any of the values 0, 1, 2, 3, ..., $n-1$. The lowest frequency of free vibration of the system is thus $\frac{c}{2\pi}\cdot 2\sin\frac{\pi}{4n+2}$, and the highest is a little less than $\frac{c}{\pi}$. When n is moderately large the lowest frequency is $\frac{\pi}{2n+1}$ times the standard mechanical frequency, and the highest is almost twice the standard mechanical frequency. The amplitude curve has therefore n maxima in the range of frequency 0 to $\frac{c}{\pi}$, in addition to the maximum at resonance frequency for the condenser circuit. Since

$$2\sin\frac{2s+1}{2n+1}\frac{\pi}{2}=1, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

when $s \doteq \frac{n}{3}$ approximately, we see that one-third of the total number of maxima occur at frequencies less than the standard mechanical frequency. At each of the successive maxima the value of the amplitude is given by

$$a_n=\frac{eEC_0}{m(d-a)D}\cdot\frac{1}{2K\omega_s}, \quad . \quad . \quad . \quad . \quad (23)$$

this being $\frac{c^2}{2nK\omega_s D}$ times the amplitude corresponding to zero frequency.

From the solution which we have obtained above it would be possible to calculate the value of the intensity of sound at any point of observation near a condenser telephone corresponding to any chosen frequency $\frac{\omega}{2\pi}$. The intensity of sound emitted at any frequency is directly proportional to the average amount of energy communicated to the air per unit of time by the upper plate of the condenser, a quantity which is to be found from the expression

$$W=\tfrac{1}{2}\rho_0 VA\omega^2 a_n^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

The curve of intensity plotted against frequency has thus a series of maxima at the same frequencies as the maxima on the amplitude curve, but, as we see from (23), at these maxima we have $a_s a_n D=\text{const.}$, and the series of crests on the intensity curve all lie on a curve represented by

$$y=\tfrac{1}{2}\rho_0 VA\,.\left\{\frac{eEC_0}{2Km(d-a)D}\right\}^2. \quad . \quad . \quad . \qquad (25)$$

The intensity curve for the condenser-telephone accordingly passes through the origin and thereafter has a succession of maxima at gradually decreasing intervals over the range of frequency from 0 to $\frac{c}{\pi}$, and the crests of the curve all lie on the curve indicated by (25) above. Illustrations of the form of this curve are obtained by squaring the ordinates of the curves given in the earlier paper, p. 506.

The effect of increasing the number of sheets in a condenser is now readily followed. As each sheet is added the first maximum on the intensity curve passes toward lower and lower frequency values followed by the second and so on, while the curve itself rises more and more rapidly near the origin. In this way the response at the low frequencies continuously improves with increase in the number of sheets. Nevertheless, owing to the high value of the standard frequency, even when the number of sheets is very large only a few of the first maxima come within the audible range of frequency, so that the variations on the intensity curve within this range are very gradual. With the first maximum at frequency 1000, the second falls near frequency 3000, and so on. In the instruments which have proved most successful in transmitting speech and music, a large number of large sheets are employed, so that the first maximum corresponding to the longest free vibration, and the maximum corresponding to electrical resonance in the condenser circuit, are both well toward the low frequency end of the audible range. The sibilants are also satisfactorily reproduced, with any desired range of low frequency sounds according to the number of sheets employed.

The above theory no doubt explains the fundamental dynamical theory of the condenser-telephone and indicates clearly the nature of the response curve and the conditions which determine the shape of the curve in any actual case. But it must be kept in mind that the conditions assumed in the analytical investigation do not represent closely the actual conditions of working of a condenser-telephone in practice. In neglecting all second-order terms we have restricted the investigation to the case where the e.m.f.'s impressed on the condenser are very small compared with the constant e.m.f. applied to its plates, whereas in some of the more important applications so far made of the condenser-telephone this condition is far from being fulfilled.

XII. *On the Specific Heat of Manganese Phosphide.*

By B. G. Whitmore, *B.Sc.* *

It is well known that, on the Weiss theory of ferro-magnetism, an additional term appears in the specific heat of a ferro-magnetic body in the region of its magnetic critical temperature, owing to the loss of magnetic potential energy. This additional term is given by the expression $\frac{1}{2J}\cdot\frac{N}{\rho}\cdot\frac{dI^2}{dT}$, where N is the constant of the Weiss internal field, and ρ is the density of the material. Weiss † and his collaborators found that the specific heat varied in accordance with the above theory in the case of iron, nickel, cobalt, and magnetite. Sucksmith and Potter ‡ examined the behaviour of nickel and Heusler alloys by a much more accurate method than that used by Weiss, but their results showed considerable differences from those expected on the above theory. Recently, Bates § examined the behaviour of the specific heat of a substance consisting of equal parts of manganese and arsenic. From his experiments it was not decisively settled whether the large changes in the specific heat in the neighbourhood of the magnetic critical point depended on dI^2/dT or upon dI/dT, *i.e.*, whether they were due to changes in internal magnetic energy, as Weiss supposed, or to a transformation with absorption of heat, from a magnetic to a non-magnetic state of the substance. The present experiments, which were suggested by Dr. L. F. Bates, were made to determine the behaviour of the specific heat of a ferro-magnetic material consisting of approximately equal parts of manganese and phosphorus.

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* Communicated by Prof. A. W. Porter, F.R.S.

† Weiss and Beck, *Journ. de Physique*, vol. vii. p. 249 (1908); Weiss, Piccard and Carrard, *Arch. Sci. Phys. Nat.* vol. xlii. p. 378 (1916), & vol. xliii. pp. 113 & 199 (1917).

‡ Sucksmith and Potter, Roy. Soc. Proc. A, vol. cxii. p. 157 (1926).

§ Bates, Roy. Soc. Proc. A, vol. cxvii. p. 681 (1928).

The substance was prepared as described by Hilpert and Dieckmann [*]. Pure black amorphous manganese, obtained by distilling off the mercury from an amalgam produced by the electrolysis of a solution of manganese chloride, was heated with the correct amount of red phophorus in an evacuated and sealed quartz tube to a temperature of 600° C. for ten to twelve hours. The resulting substance was digested with hydrochloric acid for several days, washed, crushed, and dried. The composition of the material, which was kindly determined for us by Mr. H. Terry and Mr. Jahn, was very approximately 66 parts by weight of manganese to 34 of phosphorus.

The specific heat measurements were made by a modification of the Nernst method [†]. The finely powdered substance was packed in a light hollow copper cylinder, containing a heating coil of No. 42 S.W.G. double silk-covered manganin wire and a resistance thermometer coil of No. 44 S.W.G. double silk-covered platinum wire. Both wires were distributed as evenly as possible throughout the powder, and leads of No. 30 S.W.G. double silk-covered copper wire passed through small holes in a tightly-fitting copper lid. The calorimeter was suspended inside a brass vessel, the leads being taken out through a glass tube sealed in with wax. The brass vessel was evacuated by a two-stage Hyvac pump, and stood in an electrically heated and well stirred bath of water. The resistance of the platinum wire was measured by means of an excellent form of Callendar and Griffith's bridge, for the loan of which I am greatly indebted to Mr. N. Eumorfopoulos. The resistance was measured directly at a series of temperatures between 0° and 30° C., some water being placed inside the brass vessel to promote conduction. A table was then drawn up, giving the temperatures corresponding to each 0·1 ohm increase in resistance.

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[*] Hilpert and Dieckmann, *Ber. der Chem. Gesell.* vol. xliv. p. 2831 (1911).

[†] *Cf.* Bates, *loc. cit.*

The temperature intervals were very nearly equal. To measure the specific heat at various temperatures a steady current, C, was passed through the manganin coil, and the times, t, at which the temperature of the resistance coil attained the above series of values, T, were noted. Then

$$(m.s+w)\,.\,\Delta T=\frac{C^2\,.\,R}{4\cdot 18}\,.\,\Delta t,$$

where m is the mass of the phosphide, s its specific heat, w the thermal capacity of the copper cylinder and the coils, and R the resistance of the heating coil. If R and ΔT were constant, as was very nearly true, any variations in specific heat would be indicated by variations in Δt. The above statement neglects loss of heat by radiation, and this was eliminated by maintaining the water bath at a temperature equal to the average temperature of each given temperature interval during the whole of the time in which the calorimeter temperature traversed that interval. Several experiments were made over the range 0° to 35° C. The behaviour of Δt was almost linear, no very pronounced maximum being observed. A slight increase was observed at about 16° C., but the experimental arrangements did not permit this increase to be measured very accurately.

The variation of the saturation magnetic intensity was measured with a sample of the same powder. Two similar copper tubes were wound with coils of No. 36 double silk-covered copper wire, which were connected in opposition. These were mounted parallel to the lines of force in the field of a Du Bois electromagnet, and they were capable of rapid rotation through 180°. One tube was filled with the powder and the other left empty. The coils were connected to a ballistic galvanometer, and the deflexions observed on rotating the tubes were recorded. Since the field used was 1960 gauss, the substance was assumed to be saturated. The tubes were surrounded by an electrically heated bath of paraffin, and experiments were made at temperatures up to 45° C., where the ballistic throw became zero. The absolute value of the intensity of magnetization was found by comparing the ballistic deflexion when the coils were connected in opposition with that due to the coil wound on the empty tube alone, the dimensions of the narrow cylinder occupied by the substance being known. No trace of a temperature hysteresis, like that obtained by Bates in the case of the arsenide, was found.

Fig. 1 shows the variation of the ballistic throw or saturation intensity I with temperature, whilst in fig. 2 are plotted both $\partial I/dT$ and $\partial I^2/\partial T$, together with the time intervals, Δt, which are a measure of the specific heat. It will be seen that the slight increase in specific heat does not exactly coincide with the maximum of either $\partial I/\partial T$ or $\partial I^2/\partial T$ in

Fig. 1.

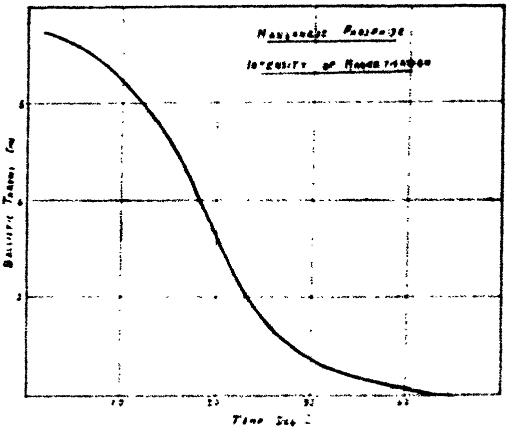
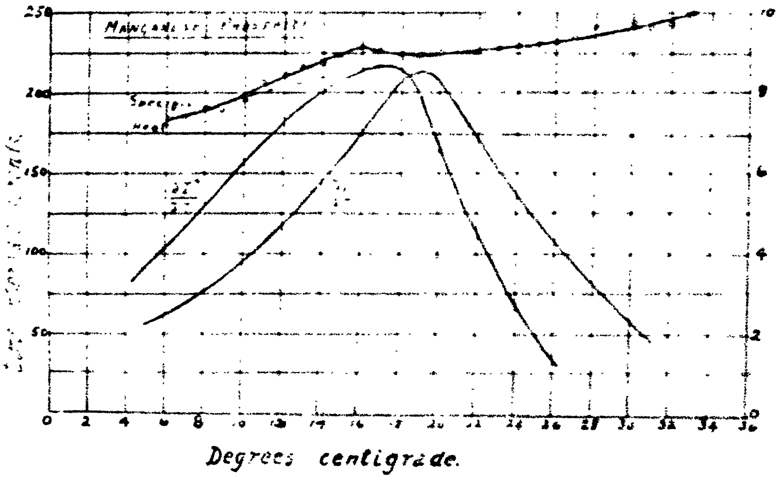


Fig. 2.



these experiments, but the general accuracy, in view of the small increase of specific heat observed, is not sufficient to enable us to state whether the difference is genuine or not. The maximum value of $\partial I/\partial T$ was 264 (e. m. u. per c.c.^{2}) per degree C. We have no information of the value of N. It was hoped to measure the paramagnetic susceptibility of the substance at higher temperatures to obtain this information, but I have not had opportunity to do so. If the specific heat curve be carried straight across as indicated by the dotted line, and the increase above this be considered as due to the loss of magnetic energy, we may calculate the value of N required on the Weiss theory to account for this increase, as we know the value of $\partial I^2/\partial T$ approximately. Calculation shows that N must be about 1500. It therefore appears that the specific heat change is of the order predicted by the Weiss theory, though apparently it does not occur exactly at the expected temperature.

Summary.

Measurements were made on the variation of specific heat of manganese phosphide in the neighbourhood of its magnetic critical temperature. A small increase in specific heat, of the order expected on the Weiss theory, was observed near the temperature at which the value of $I.\partial I/\partial T$ was a maximum, though the accuracy of the experiment was insufficient to enable us to state whether the maximum value of the specific heat coincided with the maximum value of $I.\partial I/\partial T$ or with that of $\partial I/\partial T$.

I wish to thank Professor A. W. Porter, F.R.S., for the kind interest he has taken in this work, Dr. L. F. Bates for many helpful suggestions during its course, and the Department of Scientific and Industrial Research for a grant which enabled me to carry out the experiments.

Carey Foster Laboratory,
University College, London.

III. *The Action of X-Rays on Ferrous Sulphate Solutions.*

By HUGO FRICKE, *Ph.D., and* STERNE MORSE, *Department of Biophysics, Cleveland Clinic Foundation, Cleveland, Ohio* *.

X-RAYS have an action on aqueous solutions of ferrous sulphate which causes the iron to pass from the ferrous to the ferric state. The following investigation of this reaction was made in the course of a study of the both $\partial I/dT$ and $\partial I^2/\partial T$, together with the time intervals, Δt, which are a measure of the specific heat. It will be seen that the slight increase in specific heat does not exactly coincide with the maximum of either $\partial I/\partial T$ or $\partial I^2/\partial T$ in

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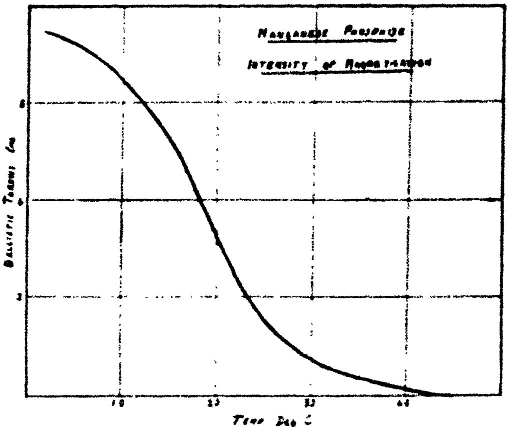

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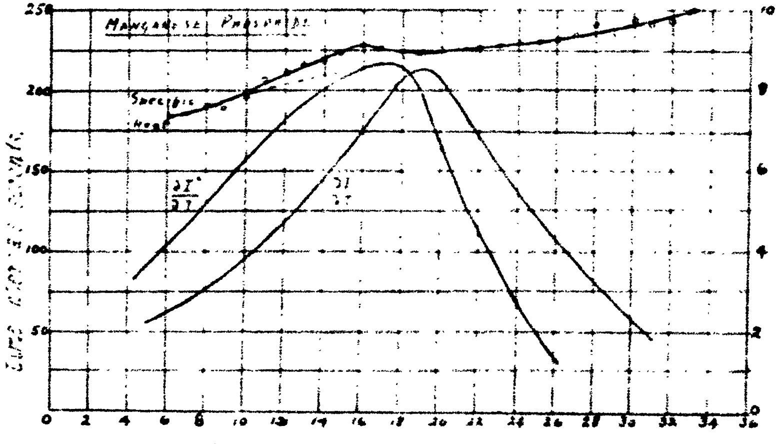

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Experimental Technique.

The X-rays were produced with a water-cooled tungsten tube made of lithium glass, a transformer and mechanical rectifier being employed. The potential was 100 K.V., the current 40 M.A.; the rays were filtered with a copper filter and a 1-mm. aluminium filter, the latter being added to absorb the characteristic rays from the copper; the thickness of the copper filter varied in different experiments between 1/10 and 5/10 mm.

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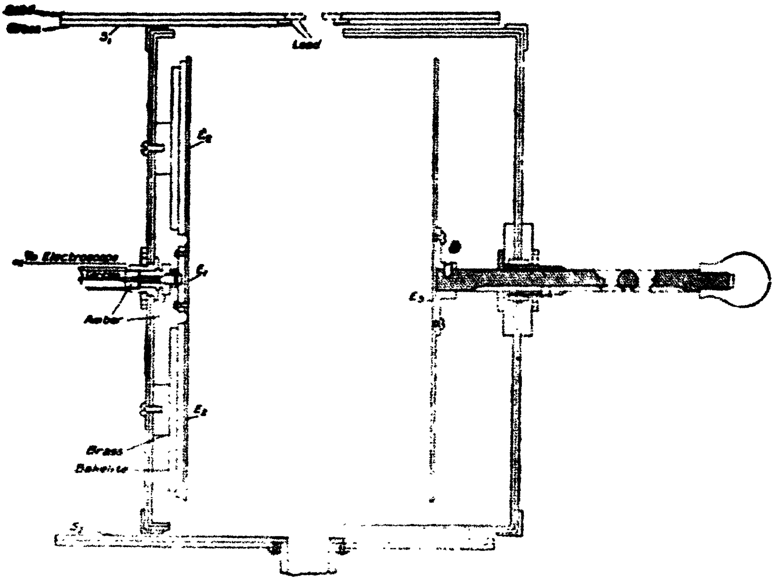

Large ionization chamber for measuring ionization in atmospheric air.

The intensity of the rays was determined by measuring the ionization produced by the rays in the chamber shown in fig. 1. The rays enter through the diaphragm in the slide S_1 and leave through the diaphragm in S_2.

The collecting electrode E_1 ($4 \cdot 98 \times 20$ cm.) is placed between the two guarding electrodes E_2 (11×20 cm.), the distance between E_1 and E_2 being ·35 mm. As the effective length of E_1 we take 5·02 cm. The wire connecting E_1 to the electrometer is placed inside a metal tube filled with ceresin. The electrode E_3 can move over 15 cm.; it is kept at such a potential as to make the electric force between E_1 and E_3 about 200 volts/cm., which is always found to be sufficient for saturation current. E_1 and E_3 are usually kept 7 cm. apart, a distance which is found to be sufficient for all irradiations to obtain the full ionization of the primary X-ray electrons. The ionization chamber is covered on the outside with 1 mm. lead except in the front, where 3 mm. is used. This is ample to protect the chamber against the small amount of stray radiation which is present in the room; when the diaphragm in the front of the chamber is closed, the electrometer does not show any observable discharge.

The ionization is determined by observing the time for the discharge of the electrometer over the length of its scale, which corresponds to a potential drop of 22·5 volts. The guarding electrodes E_2 are kept at the potential corresponding to the middle point of the scale; a change of six volts in the potential of E_2 changes the current to E_1 — about 1 per cent. when the electric force between E_1 and E_3 is 200 volts/cm.

The X-ray intensity at the front diaphragm is determined by dividing the observed ionization by the area of the front diaphragm and by the length of E_1 (5·02 cm.); diaphragms of different sizes (the diameters varying between 1/2 and 2 cm.) have been used, and it has been ascertained that the ionization current is proportional to the area of the diaphragm. All ionization measurements are corrected for variations in the density of the air due to variations in temperature and barometric pressure, air of 18° C. and 76 cm. pressure being taken as the standard reference.

As we shall see, the percentile amount of ferrous sulphate which is transformed increases in direct relation to the dilution of the solutions used. To obtain appreciable effects from the X-ray doses which it is practicable to apply, very high dilutions are required, the most dilute solutions used by us being 1/25,000 m. Furthermore, practical conditions of irradiation require that a very small amount of solution, about 1 or 2 c.c., be used. To meet these requirements, a special apparatus for electrometric titration was devised, a diagram of which is given in fig. 2. The solution to be quantitative relationship existing between chemical effects and the ionization of a gas in its dependence on the wave-length of the Röntgen rays. A full account of this study will be reported later. Some of the results obtained have already been given at a recent meeting of the American Physical Society (1).

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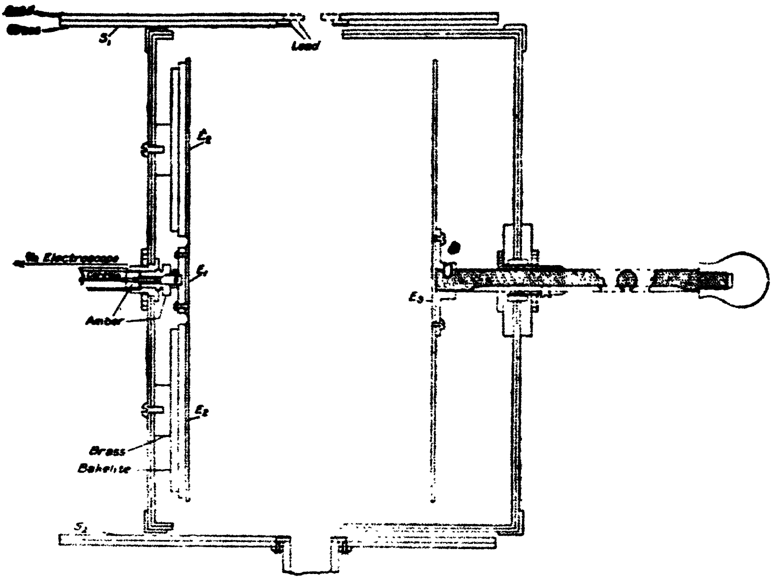

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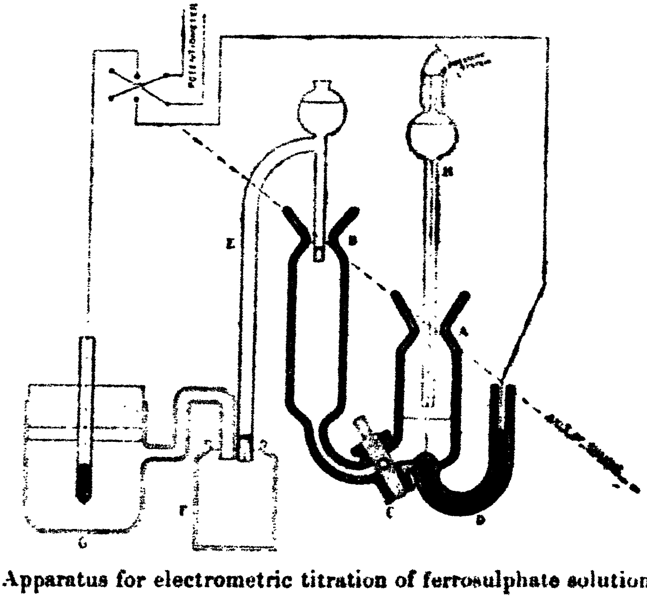
The ionization is determined by observing the time for the discharge of the electrometer over the length of its scale, which corresponds to a potential drop of 22·5 volts. The guarding electrodes E_2 are kept at the potential corresponding to the middle point of the scale; a change of six volts in the potential of E_2 changes the current to E_1 — about 1 per cent. when the electric force between E_1 and E_3 is 200 volts/cm.

The X-ray intensity at the front diaphragm is determined by dividing the observed ionization by the area of the front diaphragm and by the length of E_1 (5·02 cm.); diaphragms of different sizes (the diameters varying between 1/2 and 2 cm.) have been used, and it has been ascertained that the ionization current is proportional to the area of the diaphragm. All ionization measurements are corrected for variations in the density of the air due to variations in temperature and barometric pressure, air of 18° C. and 76 cm. pressure being taken as the standard reference.

As we shall see, the percentile amount of ferrous sulphate which is transformed increases in direct relation to the dilution of the solutions used. To obtain appreciable effects from the X-ray doses which it is practicable to apply, very high dilutions are required, the most dilute solutions used by us being 1/25,000 m. Furthermore, practical conditions of irradiation require that a very small amount of solution, about 1 or 2 c.c., be used. To meet these requirements, a special apparatus for electrometric titration was devised, a diagram of which is given in fig. 2. The solution to be analysed is placed in the vessel A; this vessel, together with the connecting vessel B, are shaken through a few degrees at a rate of one or two hundred per minute. The axis of shaking is disposed diagonally and passes through the mouths of A and B, thus enabling the stationary capillary weight burette H and the connecting tube E to dip into the liquid in A and B. With these very dilute solutions no stable potentials can be obtained unless this shaking is done. B is separated from A by a stopcock C, which is so ground as to prevent the presence of any dead space in A. Owing to the difference in levels, any leakage through this stopcock, which is kept closed during a measurement, is towards the vessel A. The ends of E are closed by paper plugs through which slow leakage occurs from the bulb at the top of E. The comparison electrode G consists of a platinum wire which dips into a 1/10 n. solution of ferrous sulphate which is half oxidized. B, E, and F are all kept filled with a dilute solution of sulphuric acid of the same normality as that of the liquid in A and in G. It is evident that there is no possibility of any contamination of the content of either of the electrode vessels A and G by the content of the other. The solution used for

Fig. 2.



Apparatus for electrometric titration of ferrosulphate solutions.

titrating is placed in the bulb of the capillary weight burette H, the capillary of which is about ·04 mm. in diameter and about 15 cm. long. The upper end of this burette is connected to a source of air-pressure, and by regulating it, the flow of the solution with which the titration is done can be regulated. For this capillary a pressure of 100 cm. of water causes about 1 c.c. to pass per hour. We have found the titration with sodium bichromate to be more practical than that with potassinm permanganate.

The procedure of titration is as follows:—The ferrosulphate solution to be analysed is removed from the radiation cell by a bulb pipette each end of which is drawn into a capillary; and the filled pipette is weighed, its contents are emptied into A and it is re-weighed. A is shaken and the potential is measured. Somewhat more sodium bichromate is added than the amount necessary to oxidize the ferrosulphate completely, and A is again shaken. The potential rises to approximately plus 225 millivolts, and the shaking is continued until the potential remains constant. The weighed burette H containing a ferrosulphate solution is then put in place, the air-pressure being so adjusted that about 20 minutes is required for the back titration. Curiously enough, when ferrosulphate is added the potential again rises to a new maximum, where it remains fixed until just before the completion of the titration, when it begins to fall rapidly. The pressure is turned off and the titration finished with only the flow from the pipette, which is due to the hydrostatic pressure. At plus 150 millivolts the weight burette is rapidly removed, placed in the horizontal position, wiped dry, and again weighed.

In this investigation the ferrosulphate solutions contained 0·8 n. sulphuric acid prepared from Grasselli's best grade of acid. The water used was distilled from alkalin permanganate in pyrex glass, and its conductivity was controlled by a cell fused to the end of the condenser. This conductivity averaged $1-2 \times 10^{-6}$ ohms. Merck's Blue Label ferrosulphate was used. The titer of the bichromate solutions used was controlled by titration with a 1/10 n. solution of ferrosulphate, which was standardized with sodium oxalate. The bichromate used was re-crystallized from Baker's Analysed Grade. All normalities given were determined by weight of solution and not by volume.

The values for the ferrous ion concentration of the radiated solution as determined from the titration and from the oxidation reduction potential of the solution agree very satisfactorily. Table I. gives the values obtained by the two methods for a 0·00100 n. solution. This good agreement shows that the radiated ferrous sulphate solutions do not contain any appreciable amount of substances other than the ferrous sulphate, which can be oxidized by sodium bichromate. We have chosen to use the values obtained from the titration because they can be reproduced somewhat better than can the values obtained from the oxidation reduction potentials.

Table I.

Action of X-rays on ·00100 m. Ferrous Sulphate in ·8 n. Sulphuric Acid. A comparison of results obtained from titration oxidation, reduction potential of radiated solution.

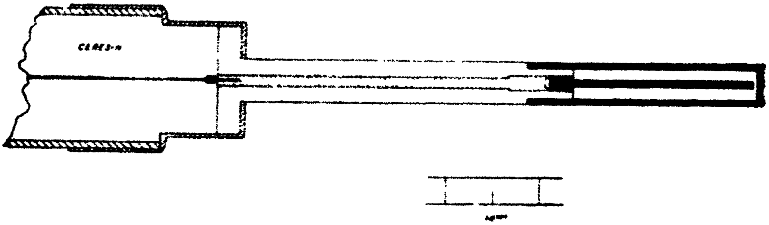
Dose (arbitrary units).	Oxidation-reduction potential of radiated solution (millivolts).	Ferrous sulphate concentration in per cent. of original concentration from	
		Titration.	Potential.
7·1	−30·2	77·0	76·8
18·1	− 7·4	57·0	57·2
20·9	+19·0	31·7	31·9
27·5	+51·3	11·8	11·6
30·7	+70·0	7·0	5·8
36·7	+64·7	7·8	7·1
42·3	+80·3	5·2	3·8

The cell in which the solution was kept during radiation was made of a plane piece of glass into which a hole was drilled. This was covered on both sides with thin cover glasses (·10 mm. thick). The cell was made air-tight by applying a small amount of melted vaseline along the edges of the cover glasses. Cells which varied in respect to area and thickness have been used.

The cell was usually placed about 20 cm. from the target of the X-ray tube, the width of the X-ray beam being regulated so as to be a few millimetres wider than the diameter of the cell.

The X-ray intensity during the irradiation of a cell was controlled by placing a specially constructed small ionization chamber directly beneath the cell. This chamber (fig. 3) consists of a graphite cylinder (wall thickness ·30 mm.) which is closed at one end, the other end fitting over an amber rod about 4 mm. in diameter; the inside length of the chamber is 2 cm., the inside diameter 3·5 mm. The wire connecting the electrode to the electrometer passes inside the amber rod and thereafter inside a metal tube filled with ceresin. The small chamber was for each type of radiation compared with the large air chamber described above. The principal reason for using the small chamber is that it will measure more accurately than the large chamber that part of the X-ray intensity which is due to the rays scattered by the irradiated liquid; this scattered intensity, however, never exceeds a small percentage of the total intensity.

Fig. 3.



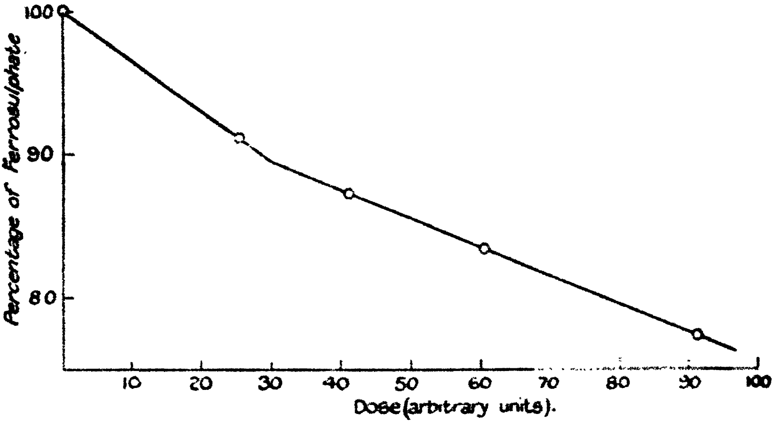
Small graphite ionization chamber.

The average X-ray intensity in the irradiated solution is obtained by multiplying by two correction factors the intensity recorded with the small chamber when the filled cell is in place. One is equal to the ratio of the X-ray intensities which are recorded when the small chamber is placed, first, at the point occupied by the centre of the cell and, secondly, in its normal position. (This differs from unity only by 1 or 2 per cent.) The absorption of the rays by the cell and by the solution is responsible for the second factor. In the present investigation the absorption of the filled cell was always so small (not exceeding 15 per cent.) that this factor, with sufficient accuracy, can be considered as equal to $\sqrt{\frac{I_2}{I_1}}$, I_1 and I_2 being the X-ray intensities recorded with and without the filled cell in place. The X-ray intensity is practically constant over the whole area of the cell.

Experimental Results.

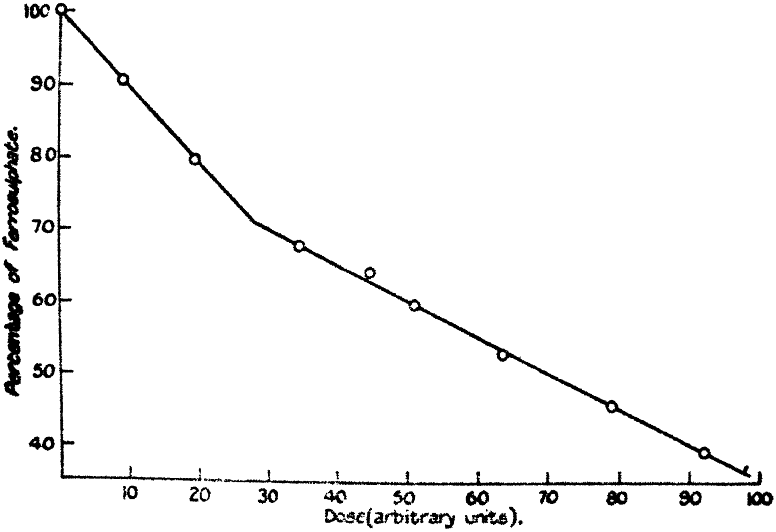
Various X-ray doses were used with various concentrations of ferrous sulphate ranging from *m*/100 to *m*/25,000. The

Fig. 4.



The action of different doses of X-rays on ·00878 m. ferrosulphate in ·8 n. sulphuric acid.

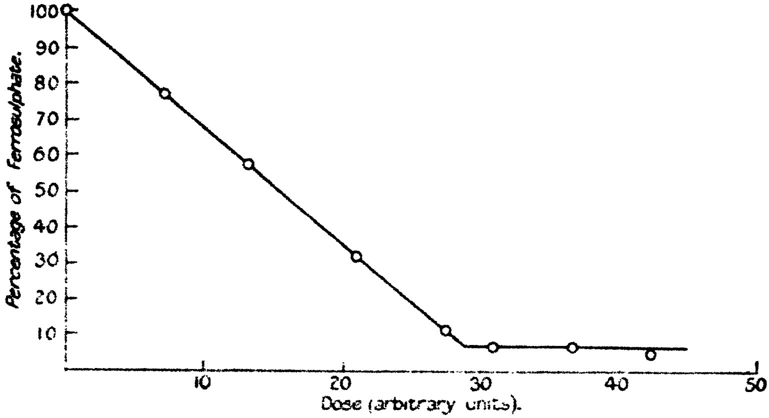
Fig. 5.



The action of different doses of X-rays on ·000337 m. ferrosulphate in ·8 n. sulphuric acid.

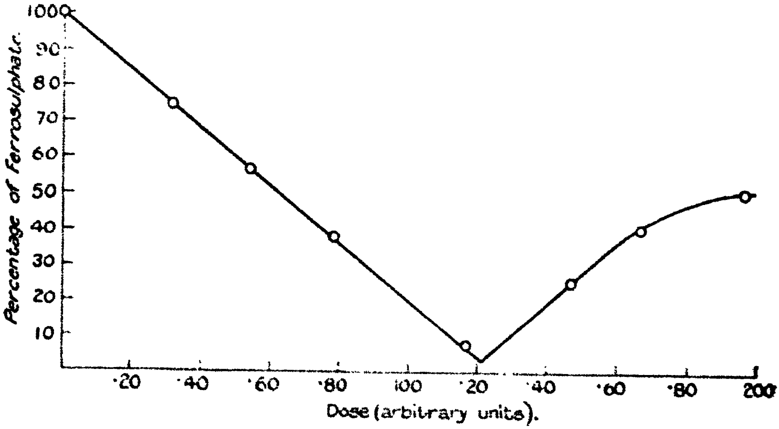
solutions were saturated with atmospheric air before irradiation and contained ·8 n. sulphuric acid. Representative results of these experiments are shown graphically in

Fig. 6.



The action of different doses of X-rays on ·00100 m. ferrosulphate in ·8 n. sulphuric acid.

Fig. 7.



The action of different doses of X-rays on ·0000406 m. ferrosulphate in ·8 n. sulphuric acid.

figs. 4–7, in which the X-ray dose is measured by the ionization produced in 1 c.c. of atmospheric air at 18° C. and 76 cm. pressure; the ionization is expressed in an arbitrary unit which is equal to 1800 electrostatic units.

For all solutions the graphs show an entirely linear relationship so long as a certain dose (29·0) is not exceeded, and within this range the absolute amount of ferrous sulphate transformed for a certain dose is independent of the concentration. Table I. gives, for each concentration used, the dose required within this range to change the concentration of the ferrous sulphate at the rate of one gram molecule in 1000 grams. When the value of the dose is in excess of 29·0, the relationship is again linear—at least as far as our measurements go, but the slope of the curve is here one-half of that present when the dose does not exceed 29·0. As we shall see presently, the number of molecules of ferrous sulphate transformed by the dose 29·0 is equal to the number of equivalents of gaseous oxygen dissolved in our solutions. This leads us to assume that the oxidation of the ferrous ions is accomplished by a reduction of the gaseous oxygen of the solution, the complete consumption of the oxygen being indicated by the discontinuity in the reaction when the dose has a value of 29·0.

Table II.

Dose required to change Concentration of Ferrous Sulphate Solutions 1 gram-molecule in 1000 grams.

Concentration (gram molecules in 1000 grams).	·00878	·00337	·00228	·00100	·000406
Dose (electrostatic units).	$5·5 . 10^6$	$5·2 . 10^7$	$5·5 . 10^6$	$5·5 . 10^6$	$5·5 . 10$

For ·8 n. sulphuric acid at 24° C., the approximate temperature at which our experiments were made, d, the Bunsen coefficient of absorption for oxygen, is 0·026 (2). The barometer pressure was, during our experiments, about 74·5 cm., and consequently the volume of absorbed oxygen (taken at 0° C. and 76 cm. pressure) for 1 c.c. of our solutions is $\frac{\cdot026 . 74\cdot5 . \cdot21}{76} = \cdot0054$ c.c.; the normality of this dissolved oxygen is $\frac{\cdot0054 \cdot 4}{22\cdot4 . 1\cdot02} = \cdot00094$ n., 1·02 being the specific density of ·8 n. sulphuric acid. Our arbitrary unit of dose equals 1800 electrostatic units, and the dose 29·0 therefore causes, according to Table II., the transformation of $\frac{1800.29}{5{\cdot}5.10^7} = {\cdot}00095$ m. ferrous sulphate. This value agrees closely with the value for the normality of the dissolved oxygen.

It appears to us that the results given above can be accounted for only by assuming that the transformation of the ferrous ions is a secondary effect, due to activated water molecules which in turn are produced by the secondary X-ray electrons. A further justification for this assumption is found if one compares the number of ferrous ions which are transformed by the absorption of a certain amount of X-ray energy with the number of pairs of gaseous ions which are produced by the absorption of the same amount of X-ray energy in air, the numbers being, as we shall see, of the same order of magnitude.

The total true absorption of X-rays by a chemical element is the sum of the photo-electric absorption and of the absorption due to the production of recoil electrons; the latter type of absorption we shall term the Compton absorption. Both are best expressed by stating the absorption of one gram electron of the substance and by defining the gram electron as the gram atom divided by the atomic number.

The chemical elements which for the most part are responsible for the X-ray absorption of atmospheric air and ·8 n. sulphuric acid respectively are so close to each other in the periodic table that no appreciable error can be introduced in the calculation of the ratio of their coefficients of absorption by assuming that the photo-electric absorption per gram electron varies as the third power of the atomic number, and that the Compton absorption per gram electron is independent of the atomic number. A calculation made in accordance with these assumptions shows that ·8 n. sulphuric acid and atmospheric air have the same coefficients of gram electron absorption.

One c.c. of atmospheric air at 18° C. and 76 cm. pressure contains $\frac{14{\cdot}45.273}{22400.291}$ gram electrons. One thousand grams of ·8 n. sulphuric acid contains 555 gram electrons. Therefore, when the same amount of X-ray energy is absorbed in the ferrous sulphate solution and in atmospheric air, and the dose does not exceed the value at which gaseous oxygen is completely consumed, the ratio of the number of ferrous ions transformed to the number of pairs of gaseous ions is $\frac{14{\cdot}45.273.2{\cdot}89.10^{14}}{555.22400.291.5{\cdot}5.10^7} = 5{\cdot}7$ (compare Table II.), the accuracy of this figure being 2 per cent. If the solution does not contain oxygen, the ratio is $\frac{5\cdot7}{2}=2\cdot8$. As we shall show in a later report, this ratio is independent of the wave-length of the rays, the range of wave-lengths investigated being ·20 to ·80 Å.U.

It is well known that by irradiation with X-rays or radio-active rays, pure water is transformed into hydrogen and oxygen. Duane and Scheuer[(8)] have determined the relation of this effect to the ionization in atmospheric air for the case of α-rays; they found that by complete absorption of α-rays in water and in atmospheric air, the ratio of the number of transformed water molecules to the number of pairs of gaseous ions is ·70. It is to be expected theoretically that this ratio will be the same for X-rays as for α-rays. We can therefore calculate the chemical effect obtained in our experiments in its relation to this effect on pure water; and we find that when a ferrous sulphate solution containing free oxygen is irradiated, $\frac{5\cdot7}{\cdot70}=8\cdot2$ ferrous ions are transformed for every water molecule which is transformed when pure water is irradiated, the same amount of X-ray energy being absorbed in both cases. $\frac{8\cdot2}{4}=2\cdot05$ oxygen molecules are reduced at the same time. If the ferrous sulphate solution does not contain free oxygen, the number of ferrous ions transformed is $\frac{8\cdot2}{2}=4\cdot1$.

It will be seen from fig. 7 that when the action on the ·0000406 m. ferrous sulphate solution has reached a point at which nearly all the ferrous ions are oxidized, an apparent reversal of the reaction takes place, the curve representing this second stage of the reaction proceeding backwards with an initial slope which is numerically equal to the slope of the line representing the first stage of the reaction. The oxidation reduction potential of the radiated solutions rises continuously with increasing doses, until for the largest dose given (1·97 in our arbitrary unit) it reaches a value of plus 145 millivolts. Evidently, when the oxidation of the ferrous ions has reached its endpoint, an equivalent quantity of a substance (perhaps hydrogen peroxide) which is oxidized by sodium bichromate accumulates in the solution. We may recall that when pure water is irradiated, in addition to hydrogen and oxygen a small quantity of hydrogen peroxide is formed. Since this substance is also destroyed by the radiation, the amount which can accumulate is limited, and it is possible that, in the dissociation of the water, hydrogen peroxide actually forms an intermediate compound. In order to obtain evidence as to whether or not the action of the X-rays on a ferrous sulphate solution may be due to a primary production of hydrogen peroxide, in a few experiments we have irradiated water or ·8 n. sulphuric acid with doses of the order of a fraction of one of our arbitrary units, and have then added the irradiated liquid to 1/4000 m. ferrous sulphate solution. The results were very irregular; as an average, effects were obtained which were about equal to the effects obtained by direct irradiation of a ferrous sulphate solution which does not contain free oxygen *.

The 0·00100 m. solution (fig. 6) does not show the apparent reversal of the reaction which we observe in the 0·0000406 m. solution. It is also noted that the X-rays do not cause a complete oxidation of the ferrous sulphate of this solution; but the reaction stops or at least proceeds very slowly when about 6 per cent. of the ferrous ions are left. A few measurements made with the stronger solutions, which are not included in the graphs, indicate that these behave in the same way. The oxidation reduction potential of the irradiated solution is apparently constant during this last stage of the reaction, the value being about 70 millivolts (see Table I.). The value of the ferrous ion concentration calculated from this potential agrees very well with the value obtained from the titration. Apparently X-rays are able to reduce the ferric ion; but it seems rather curious that the transition to the stationary part of the reaction should be as abrupt as our measurements indicate.

References.

(1) Fricke, H., "The Oxidation of Ferrous Sulphate in Aqueous Solutions by X-rays of different Wave-lengths: a determination of the Compton absorption," Phys. Rev. xxxi. p. 1117 (1928).

(2) Landolt-Börnstein, 'Physikalisch-Chemische Tabellen,' p. 770, (1923)

(3) Duane, W., and Scheuer. O., "Rescherches sur la décomposition de l'eau par les rayons *α*," *Le Radium*, x. p. 33 (1913).

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* A few irradiations have also been made of a 1/1000 n. sodium bichromate solution; the sodium bichromate is reduced. We did not attempt to obtain any high degree of accuracy in these experiments; within the experimental accuracy of about 10 per cent. the effect expressed in equivalents is equal to the effect obtained for a ferrous sulphate solution which does not contain free oxygen.

XIV. *Adsorption at the Surface of Binary Liquid Mixtures.*

By R. S. Bradley[*].

ALTHOUGH the advantage of the impartial view that neither constituent of a binary mixture is to be regarded as the "solvent" has long been recognized, undue attention has been paid to the adsorption of one constituent without at the same time considering changes in the surface concentration of the other. Thus Rideal and Schofield[†] plot

$$\frac{d\sigma}{-\mathrm{RT}d\log a_1},$$

where σ is the surface tension of alcohol-water mixtures, a_1 the activity of the alcohol, and obtain a curve showing a maximum. In reality, however, they are not plotting the surface concentration of alcohol, but

$$\Gamma_1-\Gamma_2\frac{\mathrm{N}_1}{\mathrm{N}_2},$$

where Γ_1, Γ_2 are the Gibbs's surface excesses and N_1, N_2 the mol. fractions of alcohol and water respectively.

This is easily shown:

$$d\sigma=-\mathrm{RT}\Gamma_1\,d\log a_1-\mathrm{RT}\Gamma_2\,d\log a_2,$$

$$\mathrm{O}=\mathrm{N}_1\,d\log a_1+\mathrm{N}_2\,d\log a.$$

Hence

$$\frac{-d\sigma}{\mathrm{RT}\,d\log a_1}=\Gamma_1-\Gamma_2\frac{\mathrm{N}_1}{\mathrm{N}_2}=\Gamma_1'.$$

In order to obtain Γ_1 and Γ_2, appeal must be made to some other relation, and this is given by the potential at the surface, as measured by Frumkin[‡]. The range of the interfacial forces will be considered such as to confine adsorption to the surface layer.

Considering n molecules per cm.^{2} in the surface layer, these will form a condenser of thickness $d\cos\theta$, where

$$de=\mu,$$

e being the electronic charge, μ the electric moment of the oriented molecule, θ the angle its axis makes with the normal to the surface. The charge per cm.² is ne, so that

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[*] Communicated by the Author.

[†] Rideal and Schofield, Proc. Roy. Soc. A, cxi. p. 57 (1926).

[‡] Frumkin, *Zeit. Phys. Chem.* cxi. p. 190 (1924).

$$ne = \frac{V}{4\pi d\,\overline{\cos\theta}}, \quad \mu\,\overline{\cos\theta} = \frac{V}{4\pi n},$$

where V is the surface potential. The energy of 1 sq. cm. of the surface layer, when the thickness of the condenser is $d\cos\theta$, is

$$\frac{1}{2}\,\frac{V^2}{4\pi d\cos\theta},$$

the energy per dipole

$$\frac{V^2}{8\pi d\cos\theta n} = 2\pi n\mu e\cos\theta.$$

Hence, by applying the familiar theory of dielectrics *,

$$\mu\,\overline{\cos\theta} = \mu L(a),$$

where

$$a = \frac{2\pi n\mu e}{kT}$$

and $$L(a) = \coth a - \frac{1}{a}.$$

At the surface concentrations considered, the Langevin function becomes $1 - \frac{1}{a} + 2e^{-2a}\ldots$, so that, with sufficient accuracy,

$$\Sigma n_1\mu_1\left(1 - \frac{kT}{2\pi e n_1\mu_1}\right) = \frac{V}{4\pi}.$$

If Γ_1, Γ_2 are the surface excesses in gm. mols. per cm.² of alcohol and water at molar concentrations c_1 and c_2, we shall therefore have

$$\Gamma_1\mu_1 + \Gamma_2\mu_2 = \frac{V}{4\pi N_0} - \mu_1 c_1^{\frac{2}{3}}10^{-2} - \mu_1 c_2^{\frac{2}{3}}10^{-2} + \frac{kT}{\pi e} + A,$$

where N_0 is Avogadro's number and A is a reference potential determined from the terminal condition on the alcohol side:

$$\frac{N_2}{N_1} = 0, \quad c_2 = 0, \quad V = 378 \text{ millivolts}, \quad n_1 = 7{\cdot}64.$$

The value for n_1 is calculated from the area 21·6 Å.U. for the head $-CH_2OH$ obtained from measurements on insoluble films.

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* See, for example, Debye, 'Handbuch der Radiologie,' Band vi.

Values of Γ_1 and Γ_2 calculated from the equations above are given in Table I. For Γ_1', Γ_2' Rideal and Schofield's values have been used, while μ_1 has been taken to be $1{\cdot}6\ 10^{-18}$, μ_2 $1{\cdot}7\ 10^{-18}$. Results are plotted in fig. 1: each curve shows a maximum.

Fig. 1.

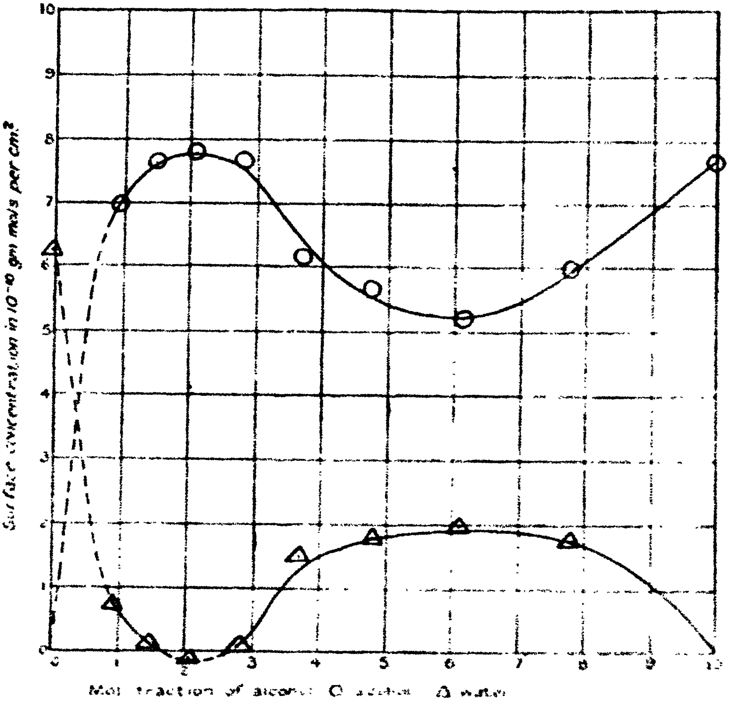


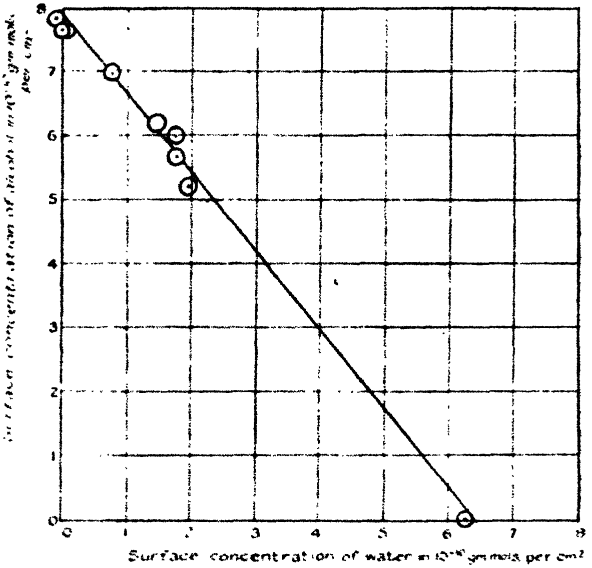
TABLE I.

N_1.	Γ_1.	Γ_2	n_1.	n_2.
·778	1·83	− ·05	5·96	1·73
·611	1·31	− ·92	5·19	1·94
·477	2·00	−1·81	5·63	1·76
·370	2·80	−3·30	6·14	1·45
·281	4·62	−5·57	7·63	·04
·207	5·18	−6·58	7·78	−·15
·144	5·42	−7·11	7·60	·11
·089	5·28	−7·34	6·97	·75

The calculation may be checked by plotting n_1 against n_2. Simple replacement would require that

$$A_1n_1+A_2n_2=1,$$

Fig. 2.



where A_1A_2 are the sectional areas of oriented alcohol and water molecules. That this relation is roughly obeyed is seen from fig. 2, the straight line giving $A_2=25{\cdot}6$ Å.U.

The University, Leeds.

XV. *On the Magnetic Susceptibility of some Amalgams and Binary Alloys.* *By* W. G. Davies, *B.Sc.*, *and* E. S. Keeping, *D.I.C.**

§ 1. *Summary.*

THE relative magnetic susceptibilities of dilute amalgams of gold, tin, indium, and gallium with respect to that of mercury have been determined by means of a Curie-Chéneveau magnetic balance⁽¹⁾. The (diamagnetic) susceptibility decreases in absolute value as the concentration of

* Communicated by Prof. E. J. Evans, D.Sc.

the dissolved metal increases, but not linearly. The effect per atom added on the susceptibility of mercury is greater for indium than for the other metals tried.

The susceptibilities of two series of binary alloys, copper-magnesium and copper-antimony, over a wide range of composition have also been determined. The susceptibility-composition curves for copper-magnesium show maxima corresponding to eutectics on the ordinary equilibrium diagram, and conspicuous minima corresponding to the known compounds $CuMg_2$ and Cu_2Mg. The equilibrium diagram for copper-antimony is more complicated, and two sets of experiments were carried out, one on the alloys prepared in the ordinary way and the other on specimens which had been carefully annealed. In all cases annealing increases the susceptibility, but the effect is very marked in the region from 20 to 60 per cent. of Cu. The only compound definitely indicated on the curve for the unannealed alloy is Cu_5Sb_2, but there is evidence of Cu_2Sb in the annealed alloy. This is the change of phase that would be expected, from the equilibrium diagram, to occur on annealing. Prominent maxima on the curves again correspond to eutectics formed.

§ 2. *Experimental Details.*

The Curie-Chéneveau magnetic balance may, with suitable precautions, be made to give very consistent readings(2), so that relative measurements of susceptibility can probably be relied on to 1 in 1000, although the absolute values are known much less accurately. In these experiments the standard substance used was pure mercury, the mass susceptibility of which was found, by direct comparison with water ($k = -0{\cdot}72 \times 10^{-6}$) to be $-0{\cdot}189 \times 10^{-6}$. This agrees well with Honda's value $-0{\cdot}19 \times 10^{-6}$.(3) Owing to the uncertainty about the absolute value, a round figure of $-0{\cdot}1900 \times 10^{-6}$ was adopted for the basis of comparison.

The same volume of amalgam was used in every experiment, the required weight being calculated from the density. The concentrations used were low enough (less than 0·6 per cent.) for the density to be calculated from the known proportion of the constituents. According to Morley and Muir(4) there is little or no volume change except for tin. The densities of tin amalgams of three different concentrations have been determined by Richards and Wilson(5), and the differences between experimental and calculated values are less than 1 in 1400. Moreover, a slight error in the assumed density would produce a proportional error of the same sign in the observed deflexion, and as the ratio of deflexion to density determines, apart from minor corrections, the mass susceptibility, the effect on the calculated value of the latter would be negligible.

The most suitable suspension-wire was found, after various trials, to be phosphor-bronze, about 0·1 mm. in diameter. In the later experiments with alloys the great variations of susceptibility with composition made it necessary to use a stouter wire of platinoid (about 0·2 mm. in diameter). Careful inter-comparisons were made with the same substance on both wires. All observations were taken at room temperature. Great care was taken that the specimen under examination always occupied the same position relative to the field of the permanent magnet in the balance ; observations could then be repeated again and again with remarkable constancy, even though the specimen-tube had meanwhile been removed from the balance and replaced two or three times.

All the metals used for amalgams and alloys were the purest obtainable. The copper-magnesium alloys were prepared in the usual way and analysed electrolytically. For the susceptibility measurements they were powdered very finely in an agate mortar and introduced into the specimen-tube. Pure copper and magnesium were also examined. Finely-powdered copper was obtained by electrolysis of a copper nitrate solution under suitable conditions of current density. The densities of the various alloys were determined by means of a specific gravity bottle, benzene being used as the liquid for the Cu-Mg alloys, which are attacked by water. The masses used in each susceptibility measurement were calculated from the densities, the volume of metal being the same each time. Owing, however, to the difficulty of ensuring that the powder was always of the same degree of fineness, the apparent volume occupied by the powder in the tube possibly varied slightly. An experiment was carried out to determine the error due to this cause under extreme conditions, and it was found that the difference between the calculated susceptibilities for a very fine and a quite coarse powder amounted to 3 in 1000 ; it was estimated that the error under ordinary circumstances would be less than a quarter of this.

The copper-antimony alloys were chill-cast, and therefore formed of small crystals. Specimens were subsequently annealed at temperatures varying from 425° to 475° C. in an atmosphere of coal-gas. It has been shown by Emlyn

Stephens (6), working in this laboratory, that annealing has a marked effect on the electrical conductivity, thermo-electric height, and Hall coefficient for these alloys. Annealing was continued until it produced no further change in these properties. The compositions of the alloys were determined by dissolving them in concentrated hydrochloric acid and potassium chlorate, separating the antimony with ammonia and tartaric acid, and depositing the copper electrolytically. All the alloys were carefully tested for traces of iron, and rejected if any appeared.

§ 3. *Susceptibilities of Dilute Amalgams.*

Table I. gives the observed mass susceptibilities relative to mercury, for which k is taken as $-0·1900\times10^{-6}$.

TABLE I.

Gold ($k=-0·145\times10^{-6}$).			Tin ($k=0·025\times10^{-6}$).		
Conc.	Temp. C.	$k\times10^6$	Conc.	Temp.	$k\times10^6$
0·0536	13·0	−0·1898	0·1654	15·0	−0·1900
0·0757	14·6	−0·1895	0·2475	15·0	−0·1899
0·1193	12·7	−0·1891	0·3230	14·5	−0·1887
0·1232	13·9	−0·1890	0·3465	14·5	−0·1885
0·1869	18·0	−0·1874	0·4064	14·8	−0·1879
0·2240	17·0	−0·1864	0·4548	14·4	−0·1877
0·2505	16·0	−0·1857	0·5712	14·8	−0·1877
Indium ($k=-0·104\times10^{-6}$).			Gallium ($k=-0·225\times10^{-6}$).		
0·0264	17·5	−0·1890	0·0526	18·0	−0·1897
0·0623	18·5	−0·1886	0·0810	19·6	−0·1888
0·1049	18·6	−0·1876	0·1298	16·6	−0·1878
0·1542	17·7	−0·1861	0·1817	18·4	−0·1873
0·2266	18·4	−0·1837	0·2436	18·9	−0·1870

The values quoted for the susceptibilities of the pure metals are mean values taken from Landolt-Börnstein. The concentrations are in percentages by weight. All these amalgams, like mercury, are diamagnetic, and the value of k may be supposed practically independent of the temperature. All four metals diminish in absolute value the diamagnetic susceptibility of mercury, indium being the most effective and tin the least. The effect of tin appears to be imperceptible up to a concentration of about 0·2 per cent. by weight.

The results are shown in the accompanying curves (fig. 1).

Fig. 1.

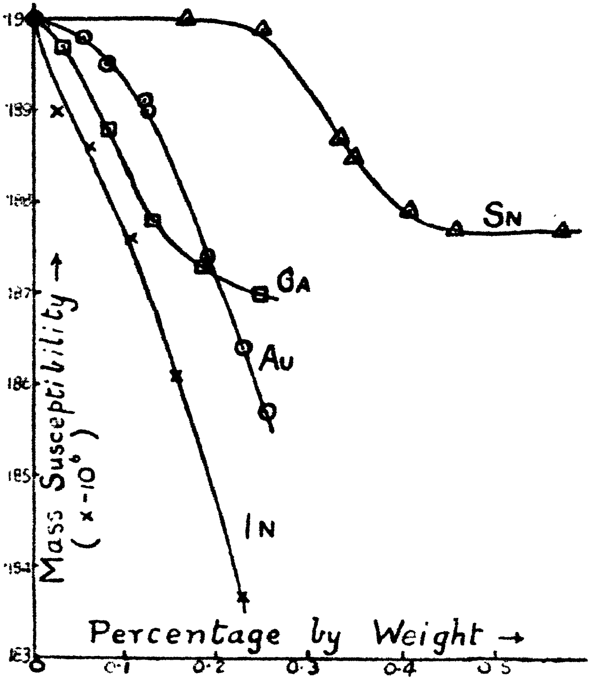


TABLE II.

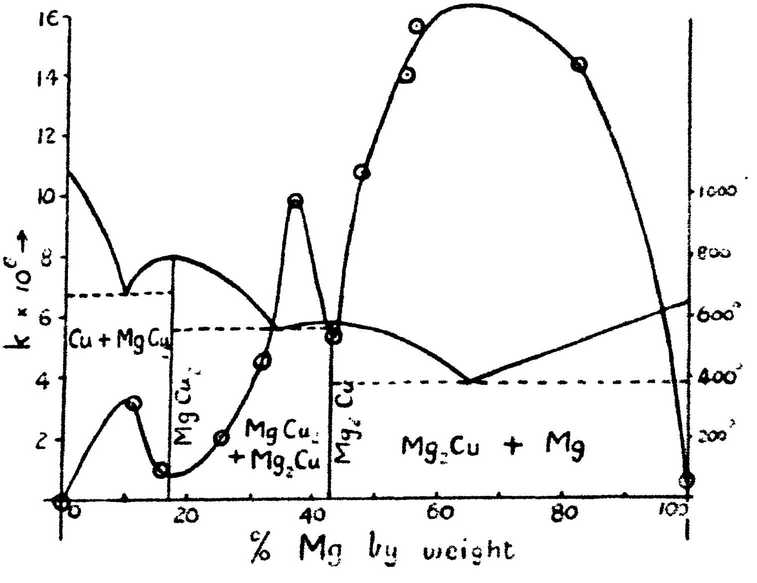
% Mg.	Density.	Temp. ° C.	$k \times 10^6$.	$k_{15} \times 10^6$.
0	8·93	22·4	−0·084	−0·084
11·0	6·64	16·3	$+3{\cdot}17_2$	$+3{\cdot}18_8$
15·7	5·69	17·0	$0{\cdot}92_2$	$0{\cdot}92_9$
25·1	5·47	18·7	$2{\cdot}04_3$	$2{\cdot}06_9$
31·6	4·62	18·9	$4{\cdot}51_4$	$4{\cdot}57_5$
36·4	3·90	17·5	$9{\cdot}76_7$	$9{\cdot}85_2$
43·0	3·58	17·4	$5{\cdot}30_1$	$5{\cdot}34_5$
47·1	3·18	17·1	$10{\cdot}67_8$	$10{\cdot}75_2$
54·2	2·98	18·9	$13{\cdot}79_9$	$13{\cdot}98_3$
55·6	2·50	15·8	$15{\cdot}56_0$	$15{\cdot}60_0$
82·2	2·25	17·5	$14{\cdot}16_4$	$14{\cdot}29_0$
100	1·74	17·8	0·559	0·564

§ 4. *Copper-Magnesium Alloys.*

All the alloys, as well as pure magnesium, were found to be paramagnetic, but copper itself is slightly diamagnetic. Table II. gives the observed susceptibilities for different compositions, and also the values corrected to a uniform temperature of 15° C. by Curie's law.

In fig. 2 the susceptibility curve for these alloys is drawn along with the equilibrium diagram (7). It is evident that eutectics are marked by maxima on the susceptibility curve, and that the two well-marked minima on these curves correspond to the compounds $CuMg_2$ and Cu_2Mg.

Fig. 2.



§ 5. *Copper-Antimony Alloys.*

Table III. gives the results for both annealed and chill-cast specimens. Although both copper and antimony are diamagnetic, all the alloys are paramagnetic. The effect of annealing is in all cases to increase the susceptibility, sometimes more than fivefold.

The relation of the susceptibility curve to the equilibrium diagram (8) is shown in fig. 3. The equilibrium diagram is more complicated than for the Cu-Mg system, and the change of phase that accompanies the annealing of the alloys with more than about 40 per cent. Cu is evident. The minima on the annealed and unannealed curves correspond respectively to compounds Cu_3Sb and Cu_5Sb_2, and there appears to be on the former curve an indication of the compound Cu_2Sb. Cu_3Sb is clearly the stable compound at the temperature of annealing. There is a very sharp maximum on both curves corresponding approximately to the eutectic at

TABLE III.

Unannealed Alloys.

% Cu.	Density.	Temp.° C.	$k\times10^{6}$.	$k\times10^{6}$.
0	6·62	22·8	−0·834	−0·834
20·5	7·15	17·4	+0·398	+0·401
29·9	7·58	17·7	0·709	+0·714
40·0	7·87	16·2	1·145	1·150
51·0	8·42	16·8	1·488	1·497
55·1	8·32	15·5	0·943	0·945
60·7	8·65	24·2	$4{\cdot}04_{4}$	$4{\cdot}17_{4}$
69·8	8·32	12·0	$13{\cdot}97_{1}$	$13{\cdot}82_{6}$
77·2	8·22	17·0	$10{\cdot}05_{2}$	$10{\cdot}11_{7}$
100	8·93	22·4	−0·084	−0·084

Annealed Alloys.

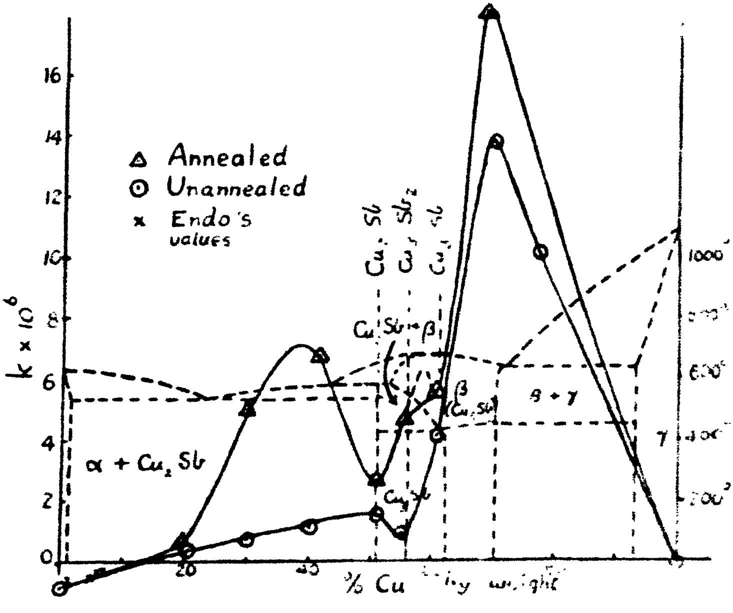
	Temp. of annealing.				
19·6	475°	7·02	18·3	+0·582	+0·589
29·8		7·45	17·8	$4{\cdot}92_{7}$	$4{\cdot}97_{5}$
41·5		7·86	17·0	$6{\cdot}69_{2}$	$6{\cdot}73_{7}$
51·0	425°	8·46	20·2	$2{\cdot}60_{1}$	$2{\cdot}64_{4}$
55·5		8·30	15·7	$4{\cdot}59_{7}$	$4{\cdot}61_{0}$
60·5		8·66	21·3	$5{\cdot}44_{3}$	$5{\cdot}56_{4}$
68·6	445°	8·34	12·5	$18{\cdot}22_{3}$	$18{\cdot}06_{5}$

71 per cent. Cu, and no trace of the eutectic at 23 per cent. Cu. In the region where annealing produces a change of phase, there is a maximum on the annealed curve at about 40 per cent. Cu and one on the unannealed curve at about 50 per cent., but it is not evident from the diagram to what states of the alloy these maxima correspond.

The copper-antimony system has been examined also by Endo (9). His tabulated values of the susceptibility relate only to alloys containing 0 to 7 per cent. Cu. These alloys are all diamagnetic, and the susceptibilities fit in fairly well with our curve, as may be seen from the values plotted. Endo gives, however, a diagram in which there is apparently a linear increase of the mass susceptibility with concentration of Cu from $-0{\cdot}539 \times 10^{-6}$ at 1·4 per cent. to about $-0{\cdot}26 \times 10^{-6}$ at 50 per cent., although he does not adduce supporting data, and his values for 5, 6, and 7 per cent. Cu if plotted do not fall anywhere near this curve.

The susceptibilities of certain of the alloys investigated are remarkably high for this class of compound. One of these (Cu-Sb, 68·6 per cent. Cu) was examined spectroscopically for traces of Fe, but no perceptible amount appeared to be present. The antimony used was stated by the firm supplying it to be 99·916 per cent. pure, the percentage of iron in it being 0·041. Since the value of the susceptibility of the antimony itself lies between those given in Landolt-Börnstein, it is evident that the presence of iron to this extent does not appreciably affect the susceptibility, and the spectroscopic examination indicates that no further iron was accidentally introduced during the process of manufacture of the alloy.

Fig. 3.



The observational work throughout has been carried out by one of us (W. G. Davies). We are deeply indebted to Prof. E. J. Evans for suggesting this research and for his continued interest.

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(2) Spencer & John, Proc. Roy. Soc. A, cxvi. p. 61 (1927).
(3) Landolt-Börnstein, p. 1202.
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(5) Richards & Wilson, *Z. phys. Chem.* lxxii. p. 141 (1910).
(6) Stephens, Univ. of Wales Thesis (to be published shortly).
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(8) I. C. T. ii. p. 437.
(9) Endo, Tôhoku Univ. Sci. Reports, No. 14, p. 479 (1925).

University College of Swansea.

XVI. *The Influence of a High Potential Direct Current on the Conductivity of an Electrolyte. By* J. A. H. Leech-Porter, *M.Sc., and* T. Alty, *D.Sc., F.Inst.P., Professor of Physics, University of Saskatchewan, Canada* *.

THE conductivity of ordinary distilled water and of dilute solutions of electrolytes is found to vary between wide limits if a high potential direct current is passed through the solution. This variation was first noted in connexion with other work, but as the effects observed were very large and, so far as we have been able to find, have not already been described, the matter has been examined more fully.

Preliminary Experiments.

A cylindrical cell 7 cm. long and 2·5 cm. in diameter and having platinum end-pieces was filled with distilled water and the resistance between the end-pieces was measured. A potential of 240 volts was then applied between the platinum plates for some minutes, after which the resistance was again measured. Usually the application of the potential increased the conductivity by about 100 per cent. On stirring the water the original resistance was restored.

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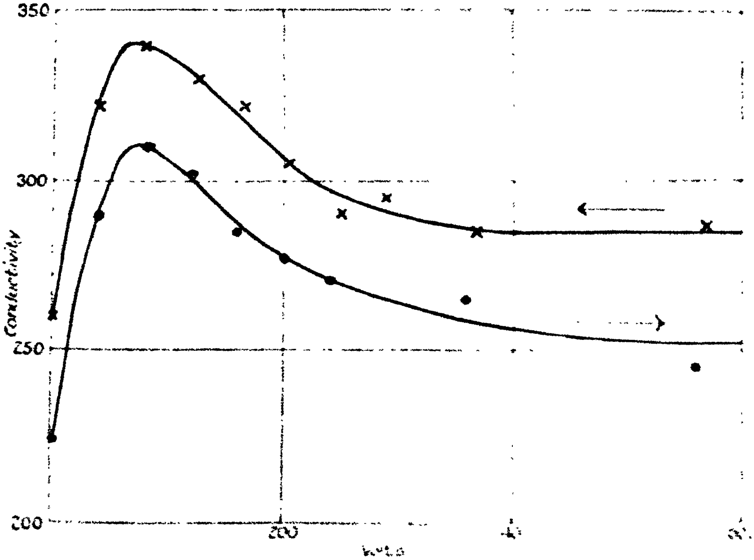
* Communicated by the Authors.

Variation of the Magnitude of the Resistance Change with Applied Voltage.

To investigate the change produced by different direct current voltages, the cell was filled with water and its resistance measured. A potential of 40 volts was then applied for ten minutes and the resistance was again measured, after which 80 volts was applied for ten minutes. This process was continued in steps of 40 volts until 600 volts in all had been applied to the cell, the resistance being measured ten minutes after each increase in voltage.

Fig. 1.



The cell was refilled with water and the experiment repeated, commencing with 600 volts, which was reduced in 40 volt steps to zero. The conductivity of the water was plotted against the applied voltage (fig. 1). In the graph the arrows indicate the order in which the points were obtained. It is seen that in the water used the change is greatest when 80 volts are applied, and that the change is independent of whether the voltage is increasing or decreasing. This independence seems to indicate that in this experiment an equilibrium state was reached between successive variations of the voltage, so that an interval between readings longer than ten minutes was not required.

In the above experiments the direct current used to produce the conductivity variations, and the alternating current used in the resistance measurements, were both applied to the same electrodes. It was therefore possible that the increased conductivity was an electrode effect. To guard against this possibility, the work was continued in a cell of different type. Two large plane electrodes were placed parallel to each other in a cylindrical glass vessel filled with a very dilute solution of HCl, and two small exploring electrodes could be introduced at any point between them. The direct current flowed between the large electrodes while the liquid resistance was measured between the small ones. In this way any possibility of the resistance change being due to the electrodes was eliminated. The resistance of the liquid at different points was measured before the D.C. was applied. After the latter had flowed for some minutes, the small electrodes were re-introduced and the measurements were repeated. It was invariably found that midway between the D.C. electrodes the resistance was very considerably greater than the normal, while close to the D.C. electrodes the resistance was greatly reduced. Stirring the water always restored the resistance to its normal value.

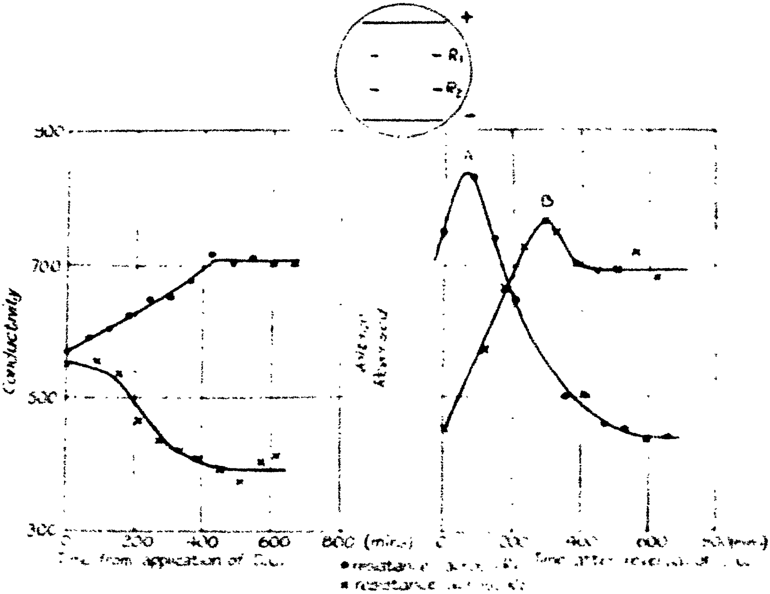
Further information was obtained by a slight modification of the above experiment. Two pairs of exploring electrodes, R_1 and R_2 (fig. 2), were kept in fixed positions and the D.C. was applied as before. The resistances across the electrodes R_1 and R_2 were measured every minute until steady values were reached. At this point the D.C. was reversed and the measurement of the resistances was continued until another pair of steady values was attained.

The arrangement of electrodes and the conductivity plotted against the time are shown in fig. 2. It will be seen that the resistance across one pair of electrodes increased while that across the other decreased. When the current was reversed, the resistances at R_1 and R_2 were interchanged. Also, on reversal, it will be noted that the conductivity at both pairs of electrodes first rises to a maximum and then falls to an equilibrium value. If the current be again reversed, this same effect is repeated.

It appears from these results that when the D.C. is applied ions of opposite sign are drawn out of the solution and collect near the two electrodes, so that an equilibrium state is set up in which the effect of diffusion is just balanced by that of the electric field. Since the conductivity of R_1 increased while that of R_2 decreased, in spite of the fact that the electrodes R_1 and R_2 were symmetrically placed with respect to the D.C. electrodes, it appears that the ions near the negative D.C. plate are held closer to it than is the case at the other electrode. This difference may be due to differences between the coefficients of diffusion of the positive and negative ions.

When the D.C. is reversed the band of Cl^- ions collected near the positive electrode will move across the cell towards R_2. The peaks A and B on the curves seem to indicate that during this movement the ions remain more or less together. When the band moves through R_1 the conductivity there (A) is a maximum. When it arrives at R_2 the latter will show a similar maximum conductivity (B). Consequently the time between the occurrence of the two maxima A and B should on this view be the time required for the Cl^- ions to move from R_1 to R_2. The H^+ ions from the negative electrode do not show this band effect.

Fig. 2.



The above results indicated fairly clearly that in a very dilute solution of a salt the application of a strong potential has the effect of drawing a number of the ions from the central region of the liquid and concentrating them near the two electrodes. In these experiments the large D.C.

electrodes were of pure aluminium sheet. In order to ensure that the presence of the aluminium was not affecting the results the cell was replaced by one in which all the electrodes were of platinum. This cell consisted of a piece of 5 mm. bore glass tubing having a platinum electrode at each end. The distance between these electrodes was about 7 cm., and a pair of exploring electrodes could be introduced through an opening about midway between them. The exploring electrodes, when not actually in use, were kept in a separate container filled with some of the same solution as that in the experimental cell. They were introduced only when a measurement of the liquid resistance midway between the D.C. electrodes was required. In this way any disturbing effect of the exploring electrodes on the distribution of the ions was avoided, and with this cell the results obtained were very consistent and reproducible. The potential was applied between the end electrodes and the resistance of the water midway between them was measured by means of the exploring electrodes and plotted against the time from the first application of the D.C.

Fig. 3.

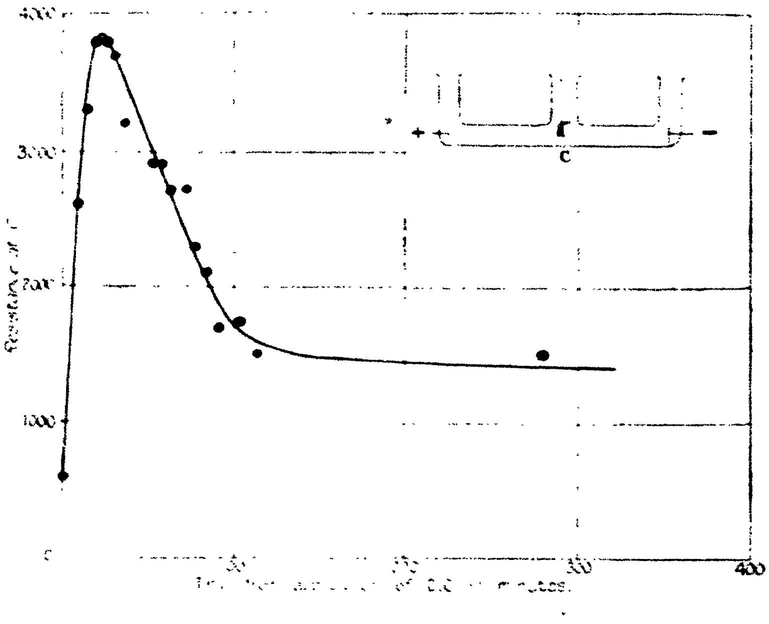
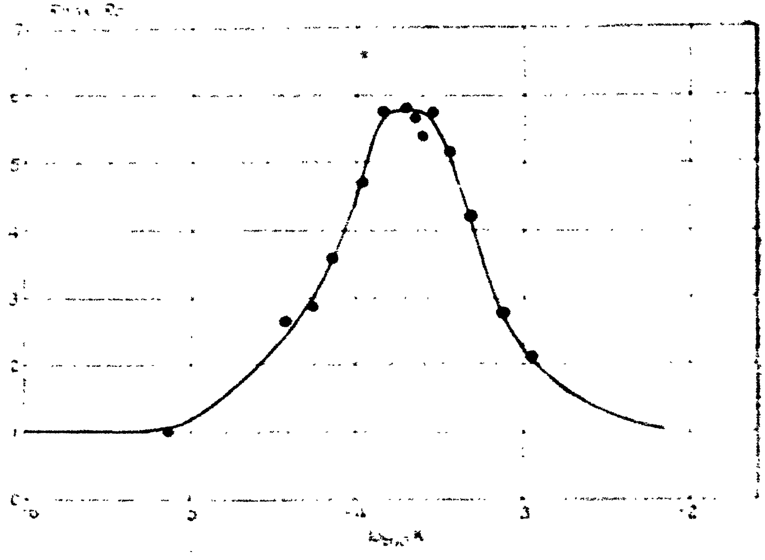


Fig. 3 is a typical graph obtained in this way. The resistance at C first rises to a sharp maximum and afterwards falls off more slowly. This seems to show that the D.C. rapidly removes the ions from the central region, and that the conductivity in this region is only afterwards increased by the diffusion of the products of electrolysis from the end electrodes. It should be noted that in all these experiments the concentrations used are very small.

Variation of the Magnitude of the Resistance Change with the Initial Conductivity of the Solution.

The magnitude of the resistance change varies with the initial conductivity of the water. This variation was investigated with the cell above described. The electrolyte used was a very dilute solution of HCl. For each value of the conductivity the graph of resistance-time for the exploring electrodes was obtained. The ratio of the maximum value of the resistance (R_{max}) to its original value (R_0) was then plotted against the logarithm of the specific conductivity (K).

Fig. 4.



The result is shown in fig. 4. For pure water, and for the more concentrated solutions of HCl, the resistance variation disappears. It rises to a maximum when the specific conductivity is about 2×10^{-4} ohm^{-1}. At this point the maximum resistance midway between the D.C. electrodes is about six times its normal value.

The foregoing experiments indicate that the ions in a completely dissociated electrolytic solution may be collected in groups near the electrodes, leaving the liquid between them almost free from ions. Under these conditions there must be a space charge around each D.C. electrode, and the uniform potential distribution between the latter is entirely destroyed. This conclusion is easily demonstrated by the use of a potentiometer to measure the potential difference between different points in the liquid.

When the D.C. potential is reversed each group of ions moves across the cell to the opposite electrode, *in the form of a band*, *i. e.*, the ions do not spread out, but cross the cell in a single group. Experiment shows that the further the group travels the more diffuse it becomes, but, if the electric field is intense, diffusion plays only a secondary part, so that the movement of the group of ions can be easily observed. Rough measurements of the velocity of the ion band, taking into account the potential variations introduced, give a value of 74×10^{-5} cm./sec./volt/cm. for the mobility of the Cl^- ion. As no special precautions were taken to control the temperature, etc., this compares satisfactorily with the accepted value of 68×10^{-5} cm./sec./volt/cm. (Kaye & Laby, 'Tables,' p. 92.).

Summary.

The conductivity of very dilute electrolytic solutions is found to vary very greatly when the electrolyte is subjected to a high potential direct current. This variation occurs only in a limited range of conductivities and is absent when the conductivity of the solution is either too high or too low. It is most pronounced in the case of HCl solutions when the specific conductivity is about 2×10^{-4} ohm^{-1}, in which case the conductivity of the liquid may vary by as much as 600 per cent.

The results are explicable on the view that the high potential draws the ions from the centre portion of the liquid towards the electrodes, where they remain. If the direct current is reversed, each of these concentrated groups of ions moves across the experimental cell as a unit. It is suggested that the ionic mobility may be determined by this method.

XVII. *The Theory of Light-Scattering in Liquids.*
By Prof. C. V. RAMAN, *F.R.S.* *

IN the July, 1928 issue of the Philosophical Magazine, Dr. Y. Rocard has made certain comments on the paper by myself and Mr. Krishnan in the Phil. Mag. for March, 1928, to which it is necessary to reply.

The outstanding facts of observation in regard to scattering of light in liquids are that while the *intensity* of scattering at the ordinary temperatures is *much smaller* in liquids in proportion to the density of the fluid than in the corresponding vapour, the *depolarization* of the transversely scattered light is *much larger*. Any theory of light-scattering to be considered reasonably successful should not only explain these facts, but also indicate the manner in which the intensity and depolarization vary when the physical condition of the fluid is altered by change of temperature or pressure. The molecular theory of light-scattering outlined by me in 1922, and more fully formulated by Dr. Ramanathan in November of the same year and published early in 1923, had precisely the foregoing for its object, and in a general way it was confirmed by the series of experimental researches carried out at Calcutta on the scattering of light by vapours and liquids at high temperatures and pressures (Proc. Roy. Soc. A, cii. p. 151, 1922, and civ. p. 357, 1923). The purpose of the paper in the Phil. Mag. for March, 1928 by Mr. Krishnan and myself was to modify the original Raman-Ramanathan theory in the light of the newer knowledge concerning the molecular structure of liquids obtained by X-ray investigations. The fundamental idea of the paper is the use, instead of the spherically symmetrical polarization field of Lorentz, of an anisotropic polarization field, the constants of anisotropy depending mainly on the geometrical form of the molecules and also on the density of the fluid. The value of our attempt is to be judged not only by the greatly improved agreement between theory and the facts of observation thus brought about, but also by the success achieved with the aid of the same idea in explaining other electrical and optical properties of liquids which have hitherto been obscure (C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. A, cxvii. pp. 1 and 589, 1927–28).

Dr. Rocard thinks that some of the conclusions set forth in the papers by Dr. Ramanathan and by ourselves had already been anticipated by Prof. L V. King. We believe that this remark has no adequate foundation. As a matter of fact, Prof. L. V. King never published any detailed theory of light-scattering in liquids. In a brief letter in 'Nature' (May 19, 1923) he put forward a conjectural amendment of the Raman-Ramanathan formula for the intensity of scattering. This was based on certain hypotheses regarding the origin of the observed depolarization in liquids, which were certainly inadmissible, as pointed out by me shortly afterwards in a letter to 'Nature' (August 4, 1923) to which no reply by Prof. King was ever published. Prof. King certainly did not contemplate the existence of the simple relationship between the observed depolarizations in liquid and vapour which forms an essential part in the Raman-Ramanathan theory; and to ascribe to him a formula for such relationship, as Dr. Rocard apparently wishes to do, would be quite unreasonable.

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* Communicated by the Author.

Dr. Rocard's note in the *Comptes Rendus* for August, 1925, to which he refers, did not contain any definite statement or proof that the polarization field within a liquid could be regarded as unaffected by the fluctuations of density, and indeed he now himself disclaims such belief. The grounds on which we, on the other hand (in agreement with Ramanathan) consider such assumption to be valid, appear to us to be of a quantitative nature. The weight of experimental evidence also seems to be in our favour.

210 Bowbazar Street, Calcutta.
August 2, 1928.

XVIII. *The Hall Effect and other Properties of the Copper-Antimony Series of Alloys.* *By* EMLYN STEPHENS, *M.Sc.* (*Wales*), *and* E. J. EVANS, *D.Sc.* (*Lond.*), *University College of Swansea* [*].

Introduction.

THE study of the variation of some electrical properties of alloys, in relation to the composition, has led to the conclusion that compounds formed of any two metals furnish singular points on a curve showing the relation between the electrical property and the composition of the alloy. This characteristic was discovered in the curve showing the relation between thermoelectric powers and concentration of one metal in an alloy by Becquerel[*] and others, while Guertler[†] found the same result when examining the changes in the electrical conductivity and the temperature coefficient of electrical resistance, in relation to composition.

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[*] Communicated by the Authors.

Smith[‡] has investigated, in addition to the phenomena already mentioned, the variations of the Hall and Nernst effects with the composition of alloys, and has observed similar singular points corresponding to compounds formed of the two metals.

The object of the present work is to obtain, for the purpose of comparison, experimental results showing the relation between the electrical resistivity, temperature coefficient of resistance, thermoelectric power, Hall coefficient, specific heat, and the composition of the copper-antimony series of alloys. These physical constants for a given alloy were in all cases determined by measurements on the same specimen.

The electrical properties of metals and alloys depend on their physical state. In the present experiments the values of the electrical resistivity and thermoelectric power were in the first place determined for the alloys after preparation, and were then redetermined for each alloy after annealing at a suitable temperature. The measurements were repeated until further annealing produced no change in these electrical properties. The temperature coefficient of resistance, specific heat, and the Hall coefficient in most cases were determined in the final state only. The Hall coefficients of Cu_2Sb and Cu_3Sb were also determined immediately after preparation of these alloys.

Kamensky[§], from determinations of the electrical conductivities of the copper-antimony series of alloys, concludes that there are two compounds, Cu_2Sb and Cu_4Sb, while Baikous[‖], from the equilibrium diagram, considers that the compounds are represented by Cu_3Sb and Cu_2Sb.

Experimental Work.

The copper used for making the alloys was of electrolytic origin, while the antimony contained ·084 per cent. of impurities. The impurities were iron ·041 per cent., lead ·025 per cent., copper ·012 per cent., sulphur ·003 per cent., and arsenic ·003 per cent. The alloys were chill cast in an iron mould in the form of plates. In considering the most suitable dimensions of the plates, attention was paid to the magnitudes of the determinations to be made. The Hall E.M.F. is usually a very small quantity, and as it varies inversely as the thickness of the plates, the latter were made as thin as possible. The great brittleness of some of the alloys prevented the preparation of satisfactory plates less than 0·4 cm. thick, and in all cases the mould was heated before pouring the alloy. The plates were approximately uniform, and the mean values of their dimensions, determined at regular intervals along them, were taken.

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[*] *Ann. de Chim. et Phys.* (4) viii. p. 408 (1866).

[†] *Zeits. für Anorg. Chem.* li. p. 397 (1906); liv. pp. 58-88 (1907).

[‡] Phys. Rev. xxx. p. 178 (1911).

[§] Phil. Mag. v. p. 270 (1884).

[‖] Landolt & Börnstein, 3rd ed. p. 800.

For these experiments ten plates were cast of the following percentage composition by weight:—(1) 80 per cent. Cu, 20 per cent. Sb; (2) 70 per cent. Cu, 30 per cent. Sb; (3) 66 per cent. Cu, 34 per cent. Sb; (4) 61·3 per cent. Cu, 38·7 per cent. Sb; (5) 55 per cent. Cu, 45 per cent. Sb; (6) 51·4 per cent. Cu, 48·6 per cent. Sb; (7) 40 per cent. Cu, 60 per cent. Sb; (8) 30 per cent. Cu, 70 per cent. Sb; (9) 20 per cent. Cu, 80 per cent. Sb; and (10) 100 per cent. Sb.

(1) *Electrical Resistivities and Temperature Coefficients of Resistance of the Alloys.*

The electrical resistivity was determined by fixing a plate of the alloy across two knife-edges, and determining the resistance of a known length by means of the Kelvin Bridge. The determinations were made at room temperature, which was measured by a thermometer placed in contact with the plate. The values of the resistivities in the initial and final states of the alloy are given in Table I. and Graph I.

TABLE I.

Composition of alloy by weight.	Resistivity before annealing, in microhms per cm.^{3}	Temperature of plate in ° C.	Resistivity after annealing, in microhms per cm.^{3}	Temperature of plate in ° C.
100 % Sb	40·9	16·0	—	—
80 % Sb 20 % Cu .	24·7	17·5	23·2	14·2
70 % Sb 30 % Cu .	18·1	17·2	17·2	14·3
60 % Sb 40 % Cu .	14·0	15·8	13·3	14·2
$SbCu_2$	11·0	15·2	11·0	13·5
45 % Sb 55 % Cu .	24·3	15·8	23·3	17·2
$SbCu_3$	77·7	18·0	99·1	15·8
34 % Sb 66 % Cu .	68·8	14·6	94·4	17·6
30 % Sb 70 % Cu .	84.0	14·1	90·1	13·8
20 % Sb 80 % Cu .	44·8	17·1	49·0	15·5
100 % Cu .	1·703	16·7	—	—

The mean temperature coefficient of resistance over the range of temperature between 0° C. and 100° C. was determined for each alloy in its final state, and these results are given in Table II. and Graph II.

GRAPH I.

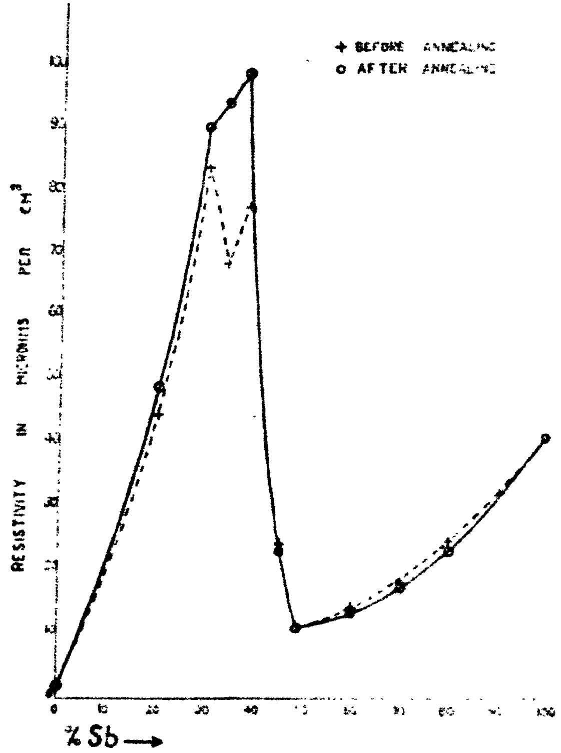


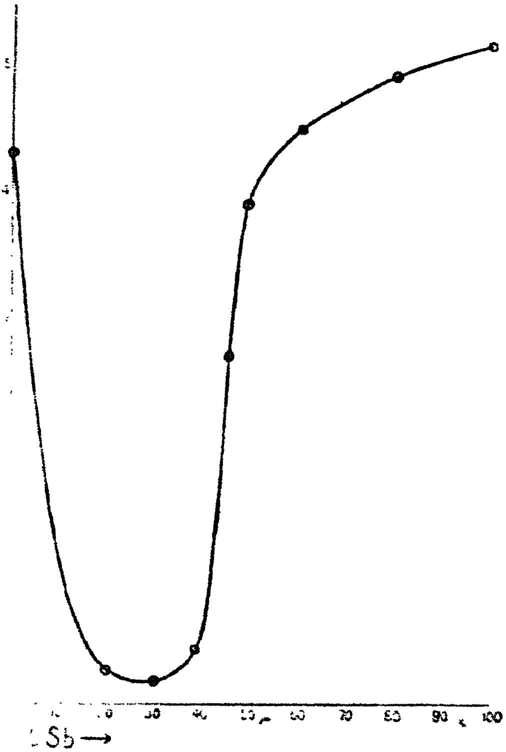
TABLE II.

Composition of alloy by weight.	Mean temp. coefficient of resistance between 0° C. and 100° C. × 10^4.
100 % Sb	51·9
80 % Sb 20 % Cu ...	49·6
60 % Sb 40 % Cu ...	45·3
$SbCu_2$	39·6
45 % Sb 55 % Cu ...	27·4
$SbCu_3$	4·33
30 % Sb 70 % Cu ...	1·81
20 % Sb 80 % Cu ...	2·59
100 % Cu ...	43·5

(2) *Thermoelectric Power of the Alloys.*

The thermoelectric properties of the alloys were examined with copper leads soldered to the ends of the plates. The copper-alloy junctions were enclosed in two jackets, by means of which one junction could be kept at the temperature of steam and the other at the temperature of running tap-water. The thermo-E.M.F. of the copper-alloy couples over this range of temperature was determined by means of a Tinsley vernier potentiometer. Repeated determinations of the thermoelectric power in micro-volts per degree centigrade when the temperature of the colder junction was varied over a range of several degrees agreed to 1 part in 500, so that the relation between E.M.F. and temperature was probably linear between room temperature and 100° C.

GRAPH II.



The thermoelectric power of copper with respect to lead was finally determined, and the thermoelectric power of the alloys in their initial and final states, with respect to lead, are given in Table III. and Graph III.

(3) *Hall Effect of the Alloys.*

The same method was employed for determining the Hall coefficient of the alloys as that fully described in an earlier paper by Miss P. Jones[*], and therefore only a brief description will be given in this paper.

When a metal plate conveying an electric current is placed in a magnetic field, so that the lines of force are normal to the conducting plate and to the direction of flow of the electric current, a transverse galvanomagnetic potential difference is set up between the edges of the plate.

It has been proved experimentally that, for a given metal, the Hall P.D. denoted by E is given in abs. units by the formula

$$E = \frac{R.H.I.}{d},$$

where H is the magnetic field in gauss, I is the current in abs. units, d is the thickness of the plate in cm., and R is the Hall coefficient.

This coefficient R depends on the temperature, and, for some metals, on the intensity of the magnetic field as well.

It is of importance to note that the effect has different signs in various metals, and the convention with regard to sign can be readily understood by reference to fig. 1 (p. 168).

The rectangle X represents the plate, and the circle Y, with the arrowheads indicating the direction of the current in the electromagnet, represents the magnetic field. The direction of the primary current is given by E F, the position of the equipotential line before the application of the field by A B, and the position of this equipotential line when the field is applied by C D. If the equipotential line C D is rotated in the direction of the current in the electromagnet, the effect is said to be positive, and if the equipotential line is rotated in the opposite direction, the effect is said to be negative. The Hall effect in antimony and copper differ in sign, antimony giving a large positive effect and copper a low negative effect.

Although the Hall effect is very large for antimony, its values for the copper-antimony alloys vary in a marked

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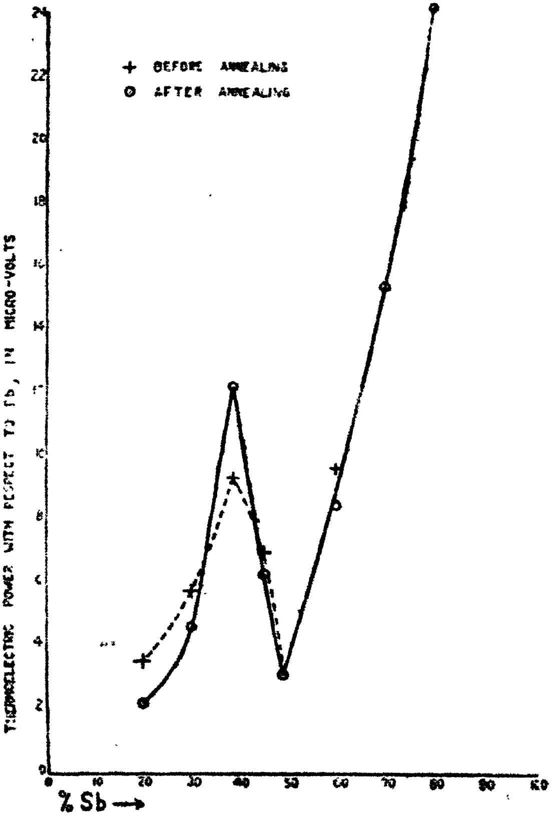
[*] Phil. Mag. (7) iv. p. 1312 (1927).

TABLE III.

Composition of alloy by weight.	Thermoelectric power with respect to Pb, in microvolts per degree centigrade. (Before annealing.)	Thermoelectric power with respect to Pb, in microvolts per degree centigrade. (After annealing.)
80 % Sb 20 % Cu ...	24·28	24·25
70 % Sb 30 % Cu ...	15·12	15·38
60 % Sb 40 % Cu ...	9·67	8·43
$SbCu_2$	3·09	3·07
45 % Sb 55 % Cu ...	6·98	6·30
$SbCu_3$	9·32	12·24
30 % Sb 70 % Cu ...	5·77	4·66
20 % Sb 80 % Cu ...	3·52	2·17

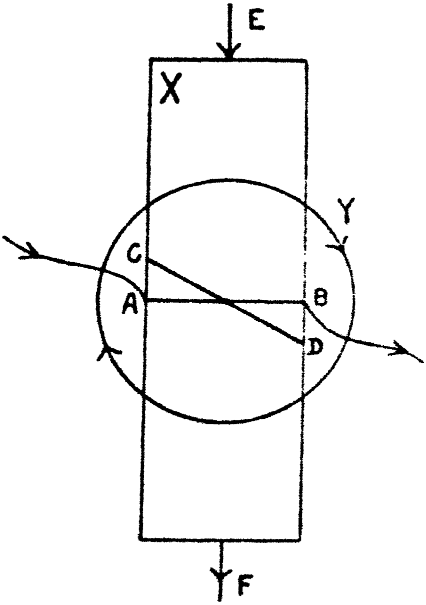
The direction of the thermoelectric force in all the alloys is such that the current flows from the alloy to the lead in the cold junction.

GRAPH III.



degree with the concentration of antimony in the alloy. The low value of the effect for some of the plates requires the use of a very sensitive galvanometer, and consequently a delicate Paschen galvanometer was used in the present experiments. It was mounted on a stone pillar, at a distance of 7½ metres from a large circular electromagnet which had been rotated into such a position that its effect on the galvanometer was a minimum. This electromagnet excited by a current of 6 amperes produced a field of 8500 gauss in the 1·5 cm. air-gap between the pole-pieces of circular section having a diameter of 9 cm.

Fig. 1.



The alloy plate under investigation was rigidly fixed in a vertical position in the magnetic field by two brass clamps which also served as leads for the primary current. These clamps were fixed to a wooden frame which also supported the secondary electrodes, consisting of spring copper contacts carried by bars of ebonite. These electrodes, which could be moved vertically along the edges of the plate by means of a screw arrangement, were connected to the galvanometer by long, well-insulated, flexible wires. These wires were pulled taut so as to eliminate the effects of vibration as far as possible.

In a determination of the Hall coefficient the secondary electrodes were adjusted on the equipotential line AB (fig. 1). Then, with the secondary circuit closed, no deflexion is produced in the galvanometer when the primary current is reversed. On applying the magnetic field and again reversing the primary current, with the secondary circuit closed, a deflexion due to the Hall P.D. between the edges of the plate is produced in the galvanometer. The Hall P.D. was determined for several values of the magnetic field up to 8500 gauss, and a graph drawn showing the relation between the P.D. and magnetic field. The value of $\frac{E}{H}$ could be determined from this graph, and the Hall coefficient calculated from the equation:

$$R = \frac{E d}{H.I.}.$$

The maximum primary current (4 amps.) passing through the plate could be read on a Weston ammeter with an accuracy of about 1 in 1200, and the minimum current (1 ampere) used at the antimony end of the series with an accuracy of about 1 in 300. The magnetic fields corresponding to various currents passing through the electromagnet were determined by a search-coil and Grassot fluxmeter. The absolute value of the magnetic field when a current of 2 amperes passed through the magnet was determined by means of a delicate ballistic galvanometer and a search-coil of known mean area, and from this result corrections could be applied to the fields as determined by the fluxmeter. The magnetic field determinations are considered to be correct within about one-half per cent.

The Hall effect was determined at room temperature, the exact temperature being observed by an accurate thermometer suspended with its bulb in contact with the plate.

The experimental results[*] for the Hall coefficients are given in Table IV. and Graph VI.

It is, however, important to point out that in addition to the Hall potential difference a transverse galvanomagnetic temperature difference is set up between the edges of the

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[*] Preliminary results on the Hall coefficients of some copper-antimony alloys in the unannealed state had already been obtained by Miss Phyllis Jones.

TABLE IV.

Composition of alloy by weight.	Thickness in cm.	Hall coefficient. before annealing.	Temp. of plate in ° C.	Hall coefficient after annealing.	Temp. of plate in ° C.
80 % Sb 20 % Cu.	·4192	—	—	+·0676	15·8
70 % Sb 30 % Cu.	·4140	—	—	+·0323	14·9
60 % Sb 40 % Cu.	·4087	—	—	+·0136	16·0
$SbCu_2$	·4140	+·00131	22·9	+·00130	21·7
45 % Sb 55 % Cu.	·4007	+·00143	21·2	+·00150	17·6
$SbCu_3$	·4166	+·00214	14·2	+·00176	14·9
30 % Sb 70 % Cu.	·4020	—	—	+·000111	18·1
20 % Sb 80 % Cu.	·4065	—	—	−·000324	22·8

GRAPH IV.

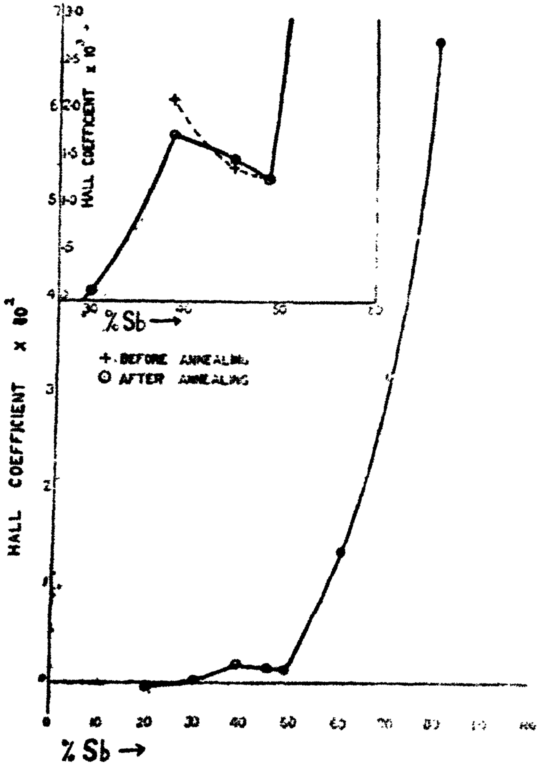


plate. This is the Ettingshausen effect and is usually very small. The difference of temperature, ΔT, is given by

$$\Delta T = \frac{P.H.I.}{d},$$

where H is the magnetic field in gauss, I the current in absolute units, *d* the thickness of the plate in cm., and P the Ettingshausen coefficient.

The Hall and Ettingshausen effects are superposed, and unless the secondary electrodes in the Hall-effect determinations are made of the same material as the plate itself, the Ettingshausen temperature difference ΔT set up between the edges of the plate will result in a thermo-E.M.F., $\theta . \Delta T$, in the secondary circuit, where θ is the thermoelectric power of the electrode with respect to the plate. Therefore the total potential difference as measured by the galvanometer in the Hall-effect determination is given by

$$E = E_H \pm \theta . \Delta T,$$

where E_H is the true Hall P.D.

Then R, the Hall coefficient becomes

$$R = \frac{E \times d}{H \times I} \pm P . \theta .$$

Generally the Ettingshausen coefficient P is very small, but the factor θ also determines whether a correction to the Hall coefficient is necessary. The secondary electrodes in the present experiments were made of copper, and some approximate determinations of $\theta . \Delta T$ were made for some of the plates.

Using constantan secondary electrodes soldered to the plate, the Ettingshausen thermo-E.M.F. was between 2 per cent. and 3 per cent. of the Hall P.D. With copper leads the Ettingshausen thermo-E.M.F. was too small to be observed with certainty, but computation from the values obtained for the deflexions due to the constantan leads showed that the Ettingshausen E.M.F. with the copper leads was less than ·5 per cent. of the Hall P.D. This is within the limits of experimental error (about 1 per cent.) of determinations of the Hall coefficients, and consequently no corrections have been made for the Ettingshausen effect in the present experiments.

(4) *The Specific Heats and Densities of the Alloys.*

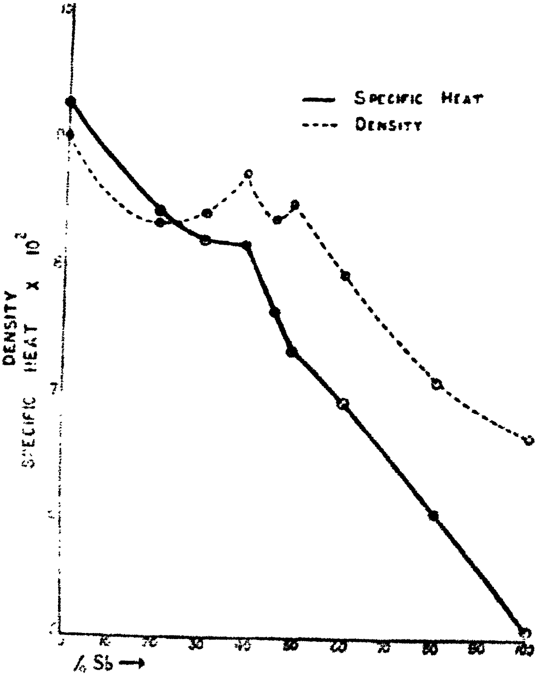
The mean specific heats of the alloys between room temperature and 100° C. were determined by means of a Joly's steam calorimeter. The determinations were repeated several times for each alloy, and agreed to within 1 per cent. The results are given in Table V. and Graph V. The results obtained by W. G. Davies* for the densities of the various alloys are also included in the same table and graph.

TABLE V.

Composition of alloy by weight.	Mean specific heat over the range of temperature indicated.	Density.
100 % Sb	·0506 (18·4° C.–100° C.)	6·62
80 % Sb 20 % Cu ...	·0599 (20·8° C.–100° C.)	7·02
60 % Sb 40 % Cu ...	·0687 (23·0° C.–100° C.)	7·86
$SbCu_2$	·0728 (21·6° C.–100° C.)	8·42
45 % Sb 55 % Cu ...	·0757 (18·9° C.–100° C.)	8·30
$SbCu_3$	·0809 (17·5° C.–100° C.)	8·66
30 % Sb 70 % Cu ...	·0812 (23·7° C.–100° C.)	8·34
20 % Sb 80 % Cu ...	·0835 (20·3° C.–100° C.)	8·26
100 % Cu ...	·0920 (19·1° C.–100° C.)	8·93

The specific heats of Cu_2Sb and Cu_3Sb have been determined by H. Schimpff † and P. Schübel ‡, the values obtained by the former being ·0739 and ·0795 respectively.

GRAPH V.



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* M.Sc. thesis on magnetic susceptibilities of amalgams and Cu-Mg and Cu-Sb alloys.

† *Zeits. phys. Chem.* lxxi. p. 257 (1910).

‡ *Zeits. anorg. Chem.* lxxxvii. p. 81 (1914).

The Annealing of the Alloys.

The chill-cast alloys were annealed at temperatures obtained from the equilibrium diagram given in the International Critical Tables, vol. ii. The annealing was performed in an electric furnace, in an atmosphere of coal-gas to prevent oxidation. The alloys were heated to their annealing temperatures very slowly, and kept at these temperatures within a few degrees for a period of about 8 hours. Then the furnace was allowed to cool to room temperature before removing the alloy. The process was repeated several times for each alloy. The temperatures at which the various alloys were annealed are given below :—

20 per cent. Cu–80 per cent. Sb	475° C.
30 ,, ,, Cu–70 ,, ,, Sb	
40 ,, ,, Cu–60 ,, ,, Sb	
Cu$_2$Sb	425° C.
55 per cent. Cu–45 per cent. Sb	
Cu$_3$Sb	
66 ,, ,, Cu–34 ,, ,, Sb	
70 per cent. Cu–30 per cent. Sb	445° C.
80 ,, ,, Cu–20 ,, ,, Sb	

The annealing of one specimen was performed with the furnace evacuated to 1 mm. pressure, and the same results were obtained as for an alloy of the same composition annealed in coal-gas.

Discussion of Results.

The three curves showing the variation of the electrical resistivity, thermoelectric power, and Hall coefficient, with the concentration of Sb in the alloy, are similar in that they have singular points corresponding to both Cu$_2$Sb and Cu$_3$Sb, and the sign of the gradients of the curves is the same for corresponding compositions. While these curves are strikingly similar in form, they are in marked contrast to the curve obtained for the variation of temperature coefficient of resistance with the composition of the alloy. The curve for the temperature coefficient of resistance has no singular points corresponding to Cu$_2$Sb and Cu$_3$Sb, but shows a point of minimum temperature coefficient corresponding to an alloy of composition near Cu$_4$Sb.

The temperature coefficient of resistance of the alloys of composition between 100 per cent. Sb and Cu$_2$Sb diminishes with the resistivity; but while the resistivity between Cu_2Sb and Cu_3Sb increases rapidly, so that the resistivity of Cu_3Sb is nine times that of Cu_2Sb, the temperature coefficient of resistance of Cu_3Sb is one-ninth that of Cu_2Sb.

The resistivity curve is not uniform between Cu_3Sb and 100 per cent. Cu, but shows a maximum value corresponding to Cu_3Sb and a sharp break corresponding to 70 per cent. Cu, 30 per cent. Sb. This irregularity at 70 per cent. Cu may be due to the hexagonal structure characteristic of Cu_3Sb extending as far as 70 per cent. Cu, 30 per cent. Sb, which nearly corresponds to Cu_4Sb.

The electrical conductivity of the copper-antimony series of alloys has been examined by N. Kurnakoff, P. Nabereznoff, and W. Ivanoff* over the range of temperature 10° C. to 600° C. While a sharply-defined maximum occurs on the isotherms of the electrical conductivity, corresponding to Cu_2Sb, no singular point is obtained corresponding to Cu_3Sb. The minimum temperature coefficient of electrical resistance, ·00014, obtained for a composition near Cu_4Sb, agrees closely with the values obtained in the present experiments, but the values of the temperature coefficients of resistance of Cu_2Sb and Cu_3Sb do not agree with the results of the present experiments. For the interval of temperature 25° C. to 100° C. the temperature coefficient of resistance of Cu_3Sb varies between the limits ·00022 and ·00112, while the coefficient for Cu_2Sb is ·00496, the corresponding values obtained in the present work being ·000433 and ·00396 respectively.

The Hall effect and thermoelectric power diminish in a similar manner as the composition of the alloy is changed from 100 per cent. Sb to Cu_2Sb. There is an increase in both effects between Cu_2Sb and Cu_3Sb, and singular points are obtained in both Curves III. and IV. corresponding to these compositions. In the range of composition between Cu_3Sb and 100 per cent. Cu the Hall effect and thermoelectric power again diminish, until corresponding to an alloy of composition 28 per cent. Sb, 72 per cent. Cu the Hall effect is zero, and changes sign with further addition of copper. Although the Hall effect for antimony is about 350 times that of copper and of opposite sign, the ratio of copper to antimony in an alloy giving zero Hall effect is as 72 : 28.

The Hall effect for pure antimony diminishes with increasing magnetic field, but in the case of the copper-antimony alloys which were examined for magnetic fields up to 8500 gauss the Hall effect was found to be independent of the magnetic field for all the alloys, except the one of composition 80 per cent. Sb, 20 per cent. Cu. In this case there is possibly a slight decrease in the value of the Hall coefficient for high fields.

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* 'Journal of the Russian Physico-Chemical Society,' Proceedings, pt. 2, xlviii. p. 701 (1916).

In Graph V., which shows the relations between the specific heat and density and percentage of antimony in the alloy, breaks occur corresponding to Cu_3Sb and Cu_2Sb, and apart from the region near Cu_3Sb, the specific heat would vary almost uniformly with the percentage of antimony in the alloy. The density curve also shows breaks corresponding to alloys of composition Cu_3Sb and Cu_2Sb.

In the present experiments annealing produced a very slight decrease in the resistivity of all the alloys of composition between Cu_2Sb and 100 per cent. Sb. In the range of composition Cu_3Sb to 100 per cent. Cu the alloys do not solidify into a single phase and a large increase in the resistivity is produced by annealing. In the chilled state the resistivity of Cu_3Sb was less than that of 70 per cent. Cu, 30 per cent. Sb, as determined by Kamensky [*].

The effect of annealing on the thermoelectric power as shown in Graph III. follows no definite order. The resistivity and thermoelectric power of Cu_2Sb are both increased by annealing, while there is a diminution of 17 per cent. in the Hall coefficient. It is of interest to note that, in these experiments, annealing produced no appreciable variation in the resistivity, thermoelectric power, and Hall effect of Cu_2Sb.

Summary.

(1) The electrical resistivity, temperature coefficient of resistance, thermoelectric power, Hall effect, specific heat, and density of the copper-antimony series of alloys have been determined.

(2) The alloys were chill-cast in the form of plates, and the electrical resistivity and thermoelectric power were determined in this state. The resistivity and thermoelectric power were redetermined after the alloys were annealed at suitable temperatures, and the process of annealing was continued until the values of these electrical properties showed no further variation. The temperature coefficient of resistance, Hall effect, specific heat and density were then

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[*] *Loc. cit.*

determined for the alloys in this final state. The Hall effects of Cu_2Sb and Cu_3Sb were also determined immediately after preparation.

(3) Singular points corresponding to both Cu_2Sb and Cu_3Sb are obtained in each of the curves showing the relation between electrical resistivity, thermoelectric power, Hall effect, specific heat, density, and the concentration of one metal in the alloy. No singular point and no evidence of the formation of compounds corresponding to Cu_2Sb and Cu_3Sb are obtained from the curve connecting the temperature coefficient of resistance and the percentage of antimony in the alloy.

(4) Annealing affected the electrical properties of the alloys to a degree depending upon their composition. Whereas the electrical properties of Cu_3Sb were greatly modified by annealing, those of Cu_2Sb remained practically unchanged.

The authors wish to thank Prof. C. A. Edwards, D.Sc., for his kindness in providing them with the materials used in this investigation, and facilities for the preparation of the alloys.

XIX. *The Analysis of Irregular Motions with Applications to the Energy-frequency Spectrum of Static and of Telegraph Signals.* By G. W. KENRICK, *Sc.D., Moore School of Electrical Engineering, University of Pennsylvania* [*].

IN his well-known paper on "Selective Circuits and Static Interference," Carson [†] has emphasized that the energy-frequency spectrum of static and the required width of frequency band furnish ultimate and inherent limitations to the advantages to be gained by the use of linear selective circuits for the elimination of interference. In his analysis, Carson considers a function $R(\omega)$ measuring the energy of the interference on the frequency corresponding to ω $(=2\pi f)$. He assumes this function to be "a continuous finite function of ω which converges to zero at infinity and is everywhere positive . . ." but does not study in detail its form for various types of random disturbances.

It is the purpose of this paper to consider this energy-frequency distribution function $R(\omega)$ further, and to indicate a method by which its form may in certain cases be computed. The methods considered are of general application, but the specific examples chosen are suggested by the researches of Appleton and Watt *. These types of pulses disclose an $R(\omega)$ varying over a wide range directly with the square of the wave-length. This result is in general accord with the early observations of Austin and was also indicated by researches of Lord Rayleigh †, in which quite different types of random disturbances were considered. A similar result is found by Wiener for still other types of random motions‡, and it seems probable that it will be found to apply to the types of disturbances important in static. An exception is, of course, to be found in the case of inductive interference from power lines and other sources produced by man and having specific and well-defined frequency characteristics.

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[*] Communicated by John R. Carson.

[†] 'Bell System Technical Journal,' April 1925.

The frequency analysis of irregular motions has for some years engaged the attention of investigators §, and its exact solution produces many troublesome problems of rigour. The function which we have to consider, if experimentally determined, is defined over perhaps a very long but always finite interval of time T. The analysis of such a set of data, while it frequently furnishes results of engineering importance, represents, mathematically, an indeterminate problem by virtue of absence of data as to the behaviour of the function before the beginning or after the end of the interval of observation. Thus, any two wholly unrelated intervals of such data (represented in graphical form) may be placed end for end and a Fourier series development derived (in terms of the total interval thus produced) which will exactly reproduce the data periodically. The practical justification for considering a frequency spectrum of such a disturbance lies in the fact that the energy-frequency distribution over any important wide band of frequencies proves little or no different, if the total interval of data or any reasonably large fraction thereof is chosen and expanded into a Fourier series in terms of a fundamental period

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* Appleton and Watt, "On the Nature of Atmospherics," Proc. Roy. Soc. A, ciii. pp. 95 and 96 (1923).

† Rayleigh, "On the Spectrum of an Irregular Disturbance," Phil. Mag. pp. 238–243 (1903); also Collected Works, v. pp. 98–102.

‡ Motion is used in this paper as a general term to denote any single valued real measurable function of a single independent variable (usually time).

§ See, for instance:—Arthur Schuster, "On Interference Phenomena," Phil. Mag. xxxvii. pp. 509–545 (June 1894), and "The Periodogram and its Optical Analogy," Proc. Roy. Soc. A, lxxxvii. pp. 136–140 (1906).

determined by its length. Each of these Fourier series developments would consist of series of terms of variable amplitudes and of frequencies equal to exact multiples of the arbitrarily chosen (and in no way inherent) base frequency, introducing the total time of observation available as one complete period. As the interval of observation grew long, however, a plot of amplitudes squared against frequency would lead to a series of lines * so closely spaced together as to give a well-defined and nearly invariable envelope. Since the exact position of the lines depends on the arbitrarily chosen fundamental period, we are inclined to associate more physical significance to the invariable envelope than to the actual lines. We choose our $R(\omega)$ curve so that the area under the curve is numerically approached by the sums of the squares of the coefficients of the terms of the Fourier development having frequencies in the same interval $\Delta\omega$. Students of probability theory will recognize this situation as exactly analogous to the representing of the probability of n events by a continuous function of n, in spite of the impossibility of the existence of a fractional number of events.

While the development in terms of a Fourier series expansion discloses the nature of the $R(\omega)$ curve, it is not always most convenient to arrive at $R(\omega)$ by Fourier series methods, and such methods are not adapted to the analysis of irregular motions not experimentally observed but defined over all time by known or assumed laws.

In this paper we shall introduce a formula derivable from the researches of Prof. N. Wiener †. By means of this formula it is possible to obtain a function $\theta(\omega)$, such that ‡

$$\theta(\omega) = \int_0^{\omega} R(\omega)d\omega. \quad . \quad . \quad . \quad . \quad (1\,a)$$

Moreover, when applied to a truly periodic function admitting a Fourier series development §, this function gives the sums of the squares of the amplitudes of the terms less than $\frac{\omega}{2\pi}$ in frequency.

Sharp lines or truly periodic disturbances of finite energy thus appear as perpendicular rises in this curve.

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* For definition of lines, see page 180.

† See Appendix A.

‡ In cases where this integral exists.

§ The formula may, however, be applied to characterise a much more general class of functions than merely those periodic in the classical sense.

1. *Development of Fundamental Formulæ.*

Specifically, then, let us consider any function $y=f(t)$ defined either analytically or graphically over a very long (or infinite) time interval T. We will assume that the mean square value of this function over a sufficiently long period approaches a definite limit [*], *i. e.*, that there exists a

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T [f(t)]^2 dt.$$

Subject to these conditions, a formula defining a function $\theta(\omega)$, having the relation to $R(\omega)$ noted in equation (1 *a*), may be shown to be[†]

$$\theta(\omega)=\frac{2}{\pi}\int_0^{\infty}\frac{\sin \omega u}{u}du\left[\lim_{K\to\infty}\frac{1}{K-u}\int_0^{K-u}f(t)f(t+u)dt\right]. \quad (1\,b)$$

While Prof. Wiener's investigations, on which the justification for this equation rests, are too extended to be summarized here, we will study some of the properties of the function $\theta(\omega)$ and show by direct computation that, when applied to a function admitting a classical Fourier series development, it leads to a function related to $R(\omega)$ in the manner described above. However, a development of the form considered by Prof. Wiener may be shown to be applicable to much more general types of functions than those admitting Fourier series developments.

The form of the graph $\theta(\omega)$ against ω $(=2\pi f)$ for a function having predominantly but not entirely random characteristics is shown in fig. 1.

Several things may be noted in regard to this function, *i. e.*:—

(1) It is monatonic, *i. e.*, it rises continuously or, at least, it never decreases.

(2) The rise between any two ω's is proportional to the energy in the spectrum of $f(t)$ over that region.

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[*] Certain other closely allied conditions are assumed, but will in most practical cases be found to exist in practice, provided we limit ourselves to functions which are nowhere infinite and possess but a finite number of finite discontinuities in a finite range.

If we also introduce the condition of periodicity, *i. e.*, that there exists a quantity p, such that for all values of t, $f(t+p)=f(t)$, our function becomes periodic in the classical sense. Our analysis applies to such functions but also to many not satisfying this condition.

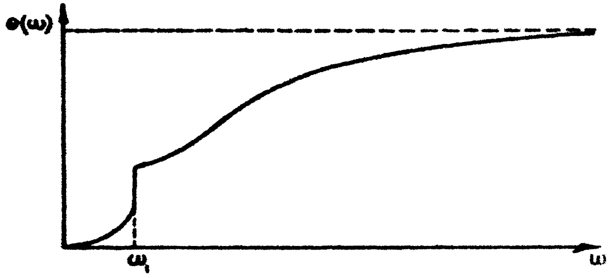
For a complete discussion of mathematical rigour, see references given in Appendix A of this paper.

[†] See Appendix A.

(3) Whenever there is a "line" in the $f(t)$ spectrum there is a sharp rise in $\theta(\omega)$, as shown at ω_1 in fig. 1. Thus we may define analytically the line components in a function not admitting a Fourier series development as that series of sinusoidal terms which, when subtracted from $f(t)$, will yield the same $\theta(\omega)$, except at that set of points at which vertical rises in $\theta(\omega)$ occur, and at these points produce a continuous $\theta(\omega)$. In practice it is never possible by the use of a finite interval of data to differentiate conclusively between merely a narrow region of rapid rise and a region in which a vertical rise occurs.

$\theta(\omega)$ is computed with the aid of a second function which is itself of no inconsiderable interest and importance. This function, which we term $\phi(u)$, represents the correlation of the original function $f(t)$ with itself under a displacement u and is the function inside the square brackets in equation (1), *i. e.*,

Fig. 1



$$\phi(u) = \lim_{K \to \infty} \frac{1}{K-u} \int_0^{K-u} f(t) f(t+u) dt. \quad . \quad . \quad (2)$$

Where $f(t)$ represents the original function under investigation, K is the total observed interval, and u is a parameter.

In the case of graphical data, the correlation function $\phi(u)$ may be fairly readily computed by mechanical means. A typical correlation curve of a function of predominantly but not wholly random characteristics is shown in fig. 2.

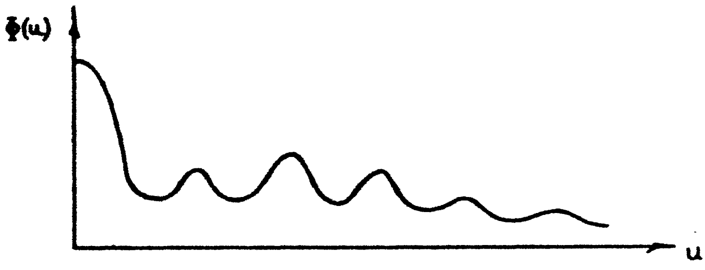
While this correlation function $\phi(u)$ is a necessity in further computations, its general form furnishes in itself considerable information of value to the investigator. Thus, we shall see presently that a "line" component in $f(t)$ leads to a $\phi(u)$ component which is sinusoidal, and hence does not decrease (except periodically) with increasing u.

The rapidity with which the correlation function $\phi(u)$ falls off with increasing u may, then, be used as a measure of the importance of disturbances not due to line components in the phenomenon under consideration.

2. *The Correlation Function $\phi(u)$ for the Special Case of a Function admitting a Fourier Series Development.*

We will now illustrate the use of the formula by applying it to a function admitting a Fourier series development. This will also serve to show the relation between $\phi(u)$ and the sums of the squares of the coefficients in this case. In applying formula (1 *b*) we have first to evaluate the quantity in brackets, which is simply the important $\phi(u)$ function already mentioned on page 180 (equation 2), *et seq.*

Fig. 2.



Thus, if we have a function $f(y)$ defined by the Fourier series,

$$f(y)=\sum_{n=1}^{n=\infty} a_n \sin(2\pi n y+\theta_n), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we have

$$\phi(u)=\operatorname*{Lim}_{K\to\infty}\frac{1}{K-u}\int_0^{K-u}\left[\sum_1^\infty a_n \sin(2\pi n y+\theta_n)\right]$$

$$\times\left[\sum_1^\infty a_m \sin 2\pi m(y+u)+\theta_m\right]dy, \quad . \quad . \quad (4)$$

$$\phi(u)=\operatorname*{Lim}_{K\to\infty}\frac{1}{K-u}\int_0^{K-u}\left[\sum_1^\infty a_n(\sin 2\pi n y\cos\theta_n+\cos 2\pi n y\sin\theta_n)\right]$$

$$\times\left\{\sum_1^\infty a_m(\sin 2\pi m(y+u)\cos\theta_m\right.$$

$$\left.+\cos 2\pi m(y+u)\sin\theta_m)\right\}dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further use of the formulæ for $\sin(a+b)$ and $\cos(a+b)$ enables us to reduce this to

$$\phi(u)=\tfrac{1}{2}\sum_{n=1}^{n=\infty}a_n^2\cos 2\pi nu. \quad . \quad . \quad . \quad . \quad (6)$$

Thus, we see that in obtaining $\phi(u)$ we have already evaluated the sums of the squares of the coefficients in the Fourier series, each multiplied by $\tfrac{1}{2}\cos 2\pi nu$. Phase differences have, moreover, been eliminated.

An interesting feature of the $\phi(u)$ curve corresponding to a "line" spectrum is its non-decreasing character, *i. e.*, its definite mean square value over an indefinitely large interval of u. A $\phi(u)$ decreasing rapidly toward zero with increasing u definitely indicates the absence of any important line components in the given function.

To verify formula (1 *b*) for $\theta(\omega)$ for this case of a Fourier series we have now merely to use equation (1 *b*), written in the form

$$\theta(\omega)=\frac{2}{\pi}\int_0^\infty\frac{\sin\omega u}{u}[\phi(u)]du. \quad . \quad . \quad . \quad (7)$$

Substituting equation (6) in (7), we have

$$\theta(\omega)=\frac{2}{\pi}\int_0^\infty\tfrac{1}{2}\sum_1^\infty\frac{a_n^2\cos 2\pi nu\sin\omega u}{u}du \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or

$$\theta(\omega)=\frac{1}{\pi}\int_0^\infty\left(\sum_1^\infty\frac{a_n^2\{\sin(\omega+2\pi n)u+\sin(\omega-2\pi n)u\}}{2u}du. \quad (9)\right.$$

It is well known that *

$$\frac{2}{\pi}\int_0^\infty\frac{\sin Ku}{u}du=\left\{\begin{array}{cc}1 & \omega>0\\ 0 & \omega=0\\ -1 & \omega<0\end{array}\right\}. \quad . \quad . \quad (10)$$

Hence

$$\theta(\omega)=\tfrac{1}{2}\sum_{s=1}^{s=n}a_s^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where

$$n<\frac{\omega}{2\pi}<n+1.$$

Thus it will be observed that in the case of a Fourier series the quantity $\theta(\omega)$ measures the sums of the squares of the amplitudes of the frequency components up to the frequency $\frac{\omega}{2\pi}$.

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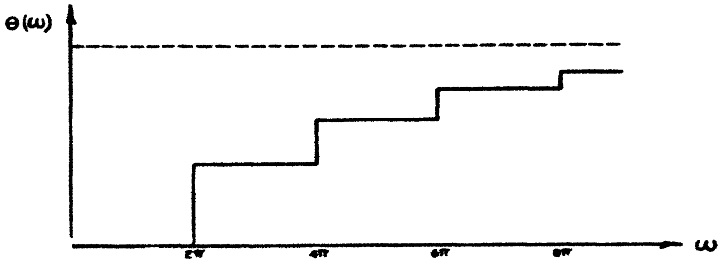
* See, for instance, Wilson's 'Advanced Calculus,' p. 366.

A typical plot of $\theta(\omega)$ for a function which admits of a Fourier series development is shown in fig. 3.

It will be noted that in this case we have a function which increases in a definite sequence of jumps at intervals of 2π. Furthermore, the asymptote of this curve is, from the well-known property of Fourier series development, equal to the mean square value of the function as defined by

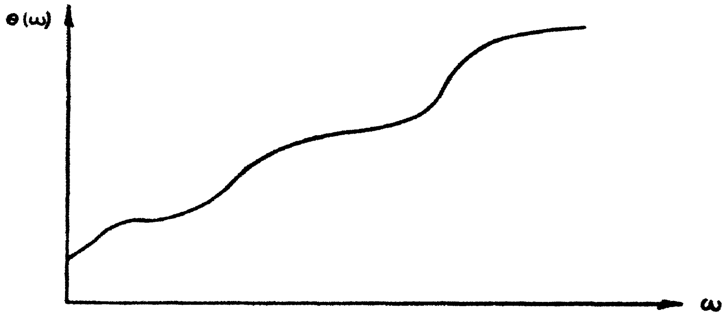
Fig. 3.



$$\lim_{K \to \infty} \frac{1}{K} \int_0^K [f(t)]^2 \, dt.$$

More generally, however, the asymptote of the $\theta(\omega)$ graph may be shown in all cases to be equal to this mean square value without regard to the nature of the $\theta(\omega)$ "spectrum"*.

Fig. 4.



Functions which do not admit of expansion into an infinite series of trigonometric terms may, however, still admit of a similar representation by means of a $\theta(\omega)$. The $\theta(\omega)$ will, however, in this case rise gradually (except, perhaps, when line components are present), as shown in fig. 4. This

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[*] Norbert Wiener, "On the Representation of Functions by Trigonometrical Integrals," *Math. Zeitschrift*, Bd. xxiv. Heft 3, pp. 578 and 581.

sort of a $\theta(\omega)$ is produced by random phenomena without periodicities.

3. *Analysis of Motions defined by Probability Considerations.*

In the preceding sections we have described a method of analysing irregular motions defined over a finite interval by means of a graph or other set of data. We will now give a simple example to show how the same formulæ may be employed to characterize irregular motion, analytically defined by probability conditions over an infinite time. We will give a few analytical examples utilizing *a priori* probabilities. The examples chosen involve hypotheses which suggest themselves for a preliminary study of such phenomena as telegraph spectra and static.

In all such cases we have somewhat different considerations in the computation of $\phi(u)$ than in the cases previously considered where the curve $f(t)$ was definitely defined for a given value of (t). In this case we compute the value of $\phi(u)$ by considering the *probability*, for a given typical value of t, that the value of $f(t)$ is in a certain range between A and $A+dA$ and the value of $f(t+u)$ is at the same time between B and $B+dB$. This gives us the compound probability that $\phi(u)=AB$, and by integration we shall have for the actual value of $\phi(u)$

$$\phi(u)=\int_{A=0}^{A=\infty}\int_{B=0}^{B=\infty} ABP(A)P(B)\,dA\,dB, \quad . \quad (12)$$

where $A=$ value of $f(t)$,

$B=$ value of $f(t+u)$,

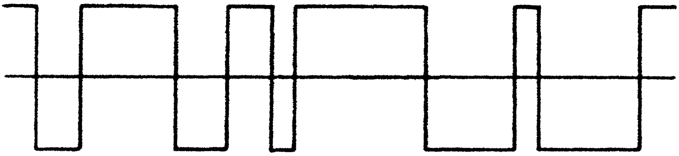
$P(A)\,dA=$ probability of value of A between A and $A+dA$,

$P(B)\,dB=$ probability of value of B between B and $B+dB$.

4. *Analysis of a certain simple Sequence of Pulses closely related to Telegraph Signals.*

We are now in a position to illustrate the application of the methods outlined above to a study of such phenomena as telegraph signals. Speaking strictly, of course, a telegraph message is not a random disturbance at all, but is exactly determined by the code, the speed, and the message. From this point of view, the energy pulses corresponding to a message of finite length could be expanded into a Fourier series with a fundamental interval equal to the length of the message. Such an analysis would, however, be laborious and would only give us a typical result as the length of the message approached infinity. We would not expect, however, long messages to differ greatly in frequency-energy distribution. In the limit this distribution would be determined by the code, the speed, and the relative probability of various letter and word combinations in the language employed. Evidently a detailed study from this point of view would be laborious indeed. In actual practice, moreover, when hand sending is employed, dots, dashes, and spaces are far from exactly equal. Investigators of this subject have gone to the other extreme of simplification in analysing a telegraph signal by considering a sequence of equally spaced dots *. Such an analysis introduces spurious lines characteristic of the assumed dot frequency, but not at all fundamental to the actual phenomena. Thus telegraph codes employ dots, dashes, and spaces ; moreover, distinction is in some cases made between the length of dashes and spaces. In automatic systems reversals of polarity are also employed. Under these conditions an assumption of a random fall of dots and dashes not necessarily of equal length would seem to approximate more closely to actual conditions.

Fig. 5.



We will first seek the periodogram analysis of such a function which shifts from $+1$ to -1 alternately at each of an infinite series of events occurring at random with an average frequency of occurrence of a events per unit time (see fig. 5).

To begin with we will require the probability that exactly n events have occurred during the interval of time t from the instant at which the arbitrary origin of time is taken ; let the probability that exactly n events have happened be $g_n(t)$ and the average frequency of occurrence be a.

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* Peters, L. J., "Behaviour of Radio Receiving Systems to Signals and to Interferences," Journ. A.I.E.E., Aug. 1926, pp. 707-716.

Then

$$\left\{\begin{array}{l}\text{Probability that zero}\\ \text{events have occurred}\\ \text{during time } t+dt\end{array}\right\}=\left\{\begin{array}{l}\text{Probability that zero}\\ \text{events have occurred}\\ \text{during the time } t\end{array}\right\}\times\left\{\begin{array}{l}\text{Probability that no}\\ \text{events occurred in}\\ \text{interval from } t \text{ to}\\ t+dt\end{array}\right\}$$

i. e., $g_0(t+dt)=g_0(t)\times(1-a\,dt)$, i. e., $\dfrac{dg_0}{dt}=-ag_0$, . (13)

or $g_0(t)=\epsilon^{-at}$. . . . . (14)

Likewise, for $n\neq0$,

$$\left\{\begin{array}{l}\text{Probability that } n\\ \text{events have occurred}\\ \text{during the time}\\ t+dt\end{array}\right\}=\left\{\begin{array}{l}\text{Probability that}\\ n-1 \text{ events have}\\ \text{occurred during the}\\ \text{time } t\end{array}\right\}\times\left\{\begin{array}{l}\text{Probability that one}\\ \text{event occurs during}\\ \text{the time } dt\end{array}\right\}$$
$$+\left\{\begin{array}{l}\text{Probability that } n\\ \text{events have occurred}\\ \text{during the time } t\end{array}\right\}\times\left\{\begin{array}{l}\text{Probability that no}\\ \text{events occur during}\\ \text{the time } dt\end{array}\right\}$$

i. e., $g_n(t+dt)=g_{n-1}(t)\{a\,dt\}+g_n(t)\{1-a\,dt\}$, . (15)

or $\dfrac{dg_n(t)}{dt}+ag_n(t)=ag_{n-1}(t)$, ... (16)

and $g_n(t)=\dfrac{a^nt^n\epsilon^{-at}}{n!}$. . . . . (17)

This result may be readily checked by substitution in the equation.

We thus have obtained in a simple manner a formula for the probability that exactly n events have occurred in a time t if the average frequency of occurrence is a.

Students of probability theory will recognize this equation as the Poisson Exponential Binomial limit widely employed by Bell System Engineers in probability computations *.

We will now utilize this result to obtain the corresponding correlation coefficient $\phi(u)$ for our random pulses.

We note that if an even number of pulses have taken place the correlation is $+1$; if an odd number take place it is -1.

We shall have, then, $\phi(u)$ equal to the sums of the probabilities that exactly zero 2, 4, 6, etc., pulses have taken place minus the probabilities that exactly 1, 3, 5, 7, etc., pulses have taken place, this gives for $\phi(u)$ †

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* See in particular, Fry, T. C., 'Probability and its Engineering Uses' (Van Nostrand, 1928).

† Equation (12) for $\phi(u)$ in this case reduces merely to a summation, as A and B may assume only integral values.

$$\phi(u)=\epsilon^{-au}+\frac{a^2u^2}{2\,!}\epsilon^{-au}+\frac{a^4u^4}{4\,!}\epsilon^{-au}+\ldots$$

$$-\frac{au}{1\,!}\epsilon^{-au}-\frac{a^3u^3}{3\,!}\epsilon^{-au}-\ldots$$

or $$\phi(u)=\epsilon^{-au}\left(1-\frac{au}{1!}+\frac{a^2u^2}{2!}-\frac{a^3u^3}{3!}+\ldots\right). \quad . \quad . \quad (18)$$

i. e., $$\phi(u)=\epsilon^{-2au}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Noting that

$$\frac{2}{\pi}\int_0^{\infty}\phi(u)\frac{\sin\omega u}{u}du=\frac{2}{\pi}\int_{u=0}^{u=\infty}du\int_{\omega=0}^{\omega=\omega}d\omega\,\phi(u)\cos\omega u,$$

we may write

$$\theta(\omega)=\frac{2}{\pi}\int_0^{\omega}d\omega\int_0^{\infty}\epsilon^{-2au}\cos\omega u\,du$$

$$=\frac{2}{\pi}\int_0^{\omega}d\omega\left[\frac{2a\,d\omega}{4a^2+\omega^2}\right]=\frac{2}{\pi}\tan^{-1}\frac{\omega}{2a}. \quad . \quad (20)$$

A plot of $\theta(\omega)$ and its derivative with respect to ω, $R(\omega)$ is shown in fig. 6. From the $\theta(\omega)$ curve (and equation 20) it will be noted that if the average duration of a pulse is $\frac{1}{a}$; half the energy is included by frequency components of frequency less than $\frac{a}{\pi}$, 90 per cent. of the energy within a frequency $7\frac{a}{\pi}$ etc. It will be noted, however, that residual energy decreases but slowly with further increase in frequency.

By noting that

$$\frac{\pi}{2}-\tan^{-1}m=\tan^{-1}\frac{1}{m},$$

and that $\tan\beta=\beta$ for small values of β, we may write

$$\underset{\omega\to\infty}{\mathrm{Lim}}\ \frac{2}{\pi}\left(\frac{\pi}{2}-\tan^{-1}\frac{\omega}{2a}\right)\rightarrow\frac{4a}{\pi\omega}. \quad . \quad . \quad . \quad (21)$$

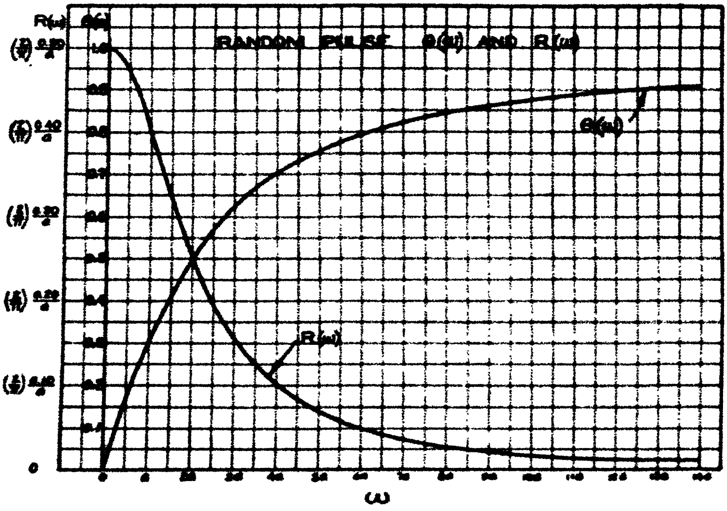
This is a very good approximation indeed when $\frac{4a}{\pi\omega}<0{\cdot}01$ so that in this case

$$[1-\theta(\omega)]\rightarrow\frac{4a}{\pi\omega}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

In other words, about 0·01 of the energy due to such a random set of pulses has a frequency greater than 130 times the average number of pulse reversals per second.

The shape of the R(ω) plot (the derivative of $\theta(\omega)$ with respect to ω) is not unlike that of a probability curve. It is of interest to note that the low frequency components receive the most energy for a given $\Delta\omega$, *i. e.*, given numerical width of frequency band. The situation is not the same, however, if the percentage width $\frac{\Delta\omega}{\omega}$ is considered. The energy in

Fig. 6.



such a band (not plotted) is proportional to $\frac{\omega}{4a^2+\omega^2}$. This function is a maximum when $\omega=2a$.

5. *The Frequency Spectrum of Static.*

Let us now consider the energy-frequency spectrum of static. Investigators of static disturbances* have disclosed that such disturbances have many of the properties of randomness which we have postulated in the previous section. Several points of departure must be considered, however, although they will prove not to be essential.

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* Appleton and Watt, *loc. cit.*

It has been pointed out by Eckersley* that radio frequency energy introduced by smooth pulses of the observed durations is insufficient to account for the magnitude of static disturbances. This analysis will afford us an opportunity to re-examine this subject from a somewhat more general point of view closely related to the work of Carson; the conclusions are in essential accord with Eckersley's, but (owing to the abruptness of the pulses considered) they indicate a radio-frequency energy at the higher wave-lengths well on the border line of modern working energies. The assumptions of randomness employed should, however, apply equally well to the ripples of the static pulses. We will now consider how static pulses and the ripples thereon depart from the assumptions made in the previous section. It will be noted that :—

(*a*) Whereas we have assumed our pulses all of the same unit amplitude, the amplitude of static pulses varies widely and could better be assumed to follow a normal Gaussian probability distribution.

(*b*) We have assumed our pulses to follow continuously one after the other.

(*c*) We have assumed our pulses to be alternately of opposite sign. Neither assumption *b* nor *c* holds without modification for static.

(*d*) The assumption of a square wave-form was suggested by Appleton and Watt originally. It would also be of interest, however, to consider an exponential form.

Assumption (*a*) is quite unessential, for we may now generalize the above problem by letting the probable amplitudes of the individual pulses vary according to a normal probability function, *i.e.*,

$$P(x) = \frac{2}{\sqrt{\pi}} \epsilon^{-x^2}$$

(letting $\kappa^2 = 1$ for simplicity, *i.e.*, measuring the departure x in mean deviations). We will consider the series of causes producing the amplitude variation as independent of those producing durations. Then equation (18) for $\phi(u)$ generalizes term for term to :—

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* Eckersley, T. L., "The Energy of Atmospherics," 'London Electrician,' p. 150 (Aug. 8, 1924). The greater amount of radio-frequency energy predicted from our analysis is due no doubt to the abrupt rise assumed for our square and exponential pulses. The form assumed by Mr. Eckersley rises gradually.

$$\phi(u)=\left(\frac{2}{\sqrt{\pi}}\right)^2\Big[\Big(\int_0^\infty \epsilon^{-x_1^2}dx_1\Big)^2\epsilon^{-au}$$
$$+\int_0^\infty\int_0^\infty \epsilon^{-x_1^2}\epsilon^{-x_2^2}\frac{a^2u^2}{2\,!}\epsilon^{-au}\,dx_1dx_2$$
$$-\int_0^\infty\int_0^\infty \epsilon^{-x_1^2}\epsilon^{-x_2^2}\frac{au}{1\,!}\epsilon^{-au}\,dx_1dx_2\ldots\Big]. \quad . \quad (23)$$

In other words the harmonic analysis of a series of pulses such as those considered is independent of the law of chance variation of their magnitudes.

In the analysis just completed, we let chance enter into the determination of the magnitudes of our pulses, but let them be alternately positive and negative. If we let chance enter into the choice of algebraic sign, either sign being equally likely for each pulse, this will dismiss (*c*). We shall have

$$\phi(u)=\frac{4}{\pi}\Big\{\Big[\int_0^\infty \epsilon^{-x_1^2}dx_1\Big]^2\epsilon^{-au}$$
$$+\tfrac{1}{2}\sum_{n=1}^{n=\infty}\frac{(au)^{2n}\epsilon^{-au}}{(2n)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\,\epsilon^{-x_1^2}\epsilon^{-x_2^2}$$
$$-(\tfrac{1}{2})\sum_{n=1}^{n=\infty}\frac{(au)^{2n}\epsilon^{-au}}{(2n)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\,\epsilon^{-x_1^2}\epsilon^{-x_2^2}$$
$$+(\tfrac{1}{2})\sum_0^\infty\frac{(au)^{2n+1}\epsilon^{-au}}{(2n+1)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\,\epsilon^{-x_1^2}\epsilon^{-x_2^2}$$
$$-(\tfrac{1}{2})\sum_0^\infty\frac{(au)^{2n+1}\epsilon^{-au}}{(2n+1)\,!}\int_0^\infty dx_1\int_0^\infty dx_2\,\epsilon^{-x_1^2}\epsilon^{-x_2^2}\Big\},$$
$$. \quad . \quad . \quad (24)$$

or $\phi(u)=\epsilon^{-au}$,

i. e., the effect of allowing a random choice of sign is to halve the frequency scale of the previous analysis, which seems reasonable from *a priori* consideration.

We may now proceed to a consideration of a general series of pulses falling individually and collectively at random, and with an average frequency of a per second. We have demonstrated that the conclusions thus derived are independent of the normal law chosen to represent the probable distribution of the amplitudes. We shall need the following simple and very interesting lemma.

Lemma.

In a series of random *independent* pulses, *equally likely to be positive or negative**, the correlation between different pulses is zero. (This property is independent of whether the pulses do or do not overlap.)

Let $f(A_1, t)dA_1$ be the probability that a certain pulse has a value of A_1 (between A_1 and A_1+dA_1, of course) at a given instant t. Now, since any pulse is equally likely to be positive or negative, $f_1(A_1t)=f_1(-A_1, t)$ for all values of t, $f_1(A_1, t)$ is an even function of A_1. Hence, $A_1f(A_1, t_1)$ is an odd function of A_1 for all values of t_1. Likewise for any other pulse $A_2f(A_2, t_2)$ is an odd function of A_2 for all values of t_2.

Now (from equation (12)) the correlation for the displacement interval (u),

$$\begin{aligned}\phi(u) &= \lim_{B\to\infty}\frac{1}{2B}\int_{t=-B}^{t=B}dt\left\{\int_{-\infty}^{\infty}dA_1\int_{-\infty}^{\infty}dA_2(A_1A_2)f_1(A_1, t)\right.\\ &\qquad\qquad\left.\times f_2(A_2, t+u)\right\}\\ &= \lim_{B\to\infty}\frac{1}{2B}\int_{t=-B}^{t=B}dt\left\{\int_{-\infty}^{\infty}A_1f_1(A_1, t)dA_1\right\}\left\{\int_{-\infty}^{\infty}A_2\right.\\ &\qquad\qquad\left.\times f_2(A_2, t+u)dA_2\right\} \quad . \quad (25)\end{aligned}$$

Since $A_1f_1(A_1, t_1)dA_1$ and $A_2f_2(A_2, t+u)dA_2$ are both *odd* functions, their integrals between $+\infty$ and $-\infty$ vanish, hence

$$\phi(u) = \lim_{B\to\infty}\frac{1}{2B}\int_{-B}^{B}dt\{0\}\{0\} = 0.$$

An important consideration, entering into the frequency characterization of static as a random sequence of pulses, is to be sure that no false basic periodicities are introduced by the choice of a definite constant duration of pulse or any but a random law of occurrence.

In the preceding discussion we have seen, then, how the frequency spectrum of a continuous sequence of pulses, initiated at random instants and of an amplitude following any normal probability law, may be determined. The frequency spectrum is continuous, and the value of $\theta(\omega)$ is indeed given by the surprisingly simple formula

$$\theta(\omega) = \frac{2}{\pi}\tan^{-1}\frac{\omega}{2a}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

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* **This theorem is not true unless this condition is fulfilled.**

where a=the average frequency of occurrence of the random pulses.

This formula, with the generalization permitted by the above discussion, is nearly, if not quite, adequate to characterize the frequency distribution of static. In the closing pages of this paper, however, we will consider the analysis for the spectrum of a series of pulses of an exponential wave form falling at random with an average frequency of occurrence of n per second. We will show that the conclusions obtained from a consideration of the square pulse wave-forms are not essentially altered. We may also show by a similar attack that the conclusions are essentially the same for a series of square pulses spaced far apart and of variable duration.

6. *Analysis of Exponential Pulses.*

In carrying out this analysis we will first compute the value of the correlation function $\phi(u)$ for a random sequence of pulses having the form $f(t)=\epsilon^{-\beta t}$ for a given value of β: this we denote by $\phi_\beta(u)$. We will then compute a mean $\phi(u)$ by letting β vary according to a normal probability law round a mean value.

We have

$$\phi_\beta(u)=\frac{nT}{T}\int_0^\infty f(t)f(t+u)dt=\frac{n\epsilon^{-\beta u}}{2\beta}\quad . \quad . \quad . \quad (27)$$

From (p. 187) we note that a $\phi(u)$ of this form will give us a

$$R_\beta(\omega)=\frac{1}{\pi}\frac{n}{\beta^2+\omega^2}\quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We will now assume a normal probability variation of the β's around a mean β_0. Then the probability of a β between β and $\beta+d\beta$;

$$P(\beta)=\frac{2\kappa}{\sqrt{\pi}}\,\epsilon^{-\kappa^2(\beta-\beta_0)^2}\,d\beta.$$

Expanding $(R_\beta(\omega)$ into a series form, and making one or two obvious changes of variable and transformations, we have

$$R_\beta(\omega)=\frac{1}{\pi}\frac{n}{\omega^2}\frac{1}{1+\frac{\beta^2}{\omega^2}}$$

$$=\frac{1}{\pi}\frac{n}{\omega^2}\left[1-\frac{\beta^2}{\omega^2}+\frac{\beta^4}{\omega^4}-\ldots\right]\quad . \quad . \quad (29)$$

Now varying the β's and noting

$$\left[\mathrm{R}(\omega)\right]_{\text{mean}} = \int_{\beta=0}^{\beta=\infty} \mathrm{R}_{\beta}(\omega)\,\mathrm{P}(\beta)\,d\beta,$$

$$\left[\mathrm{R}(\omega)\right]_{\text{mean}} = \frac{1}{\pi}\frac{n}{\omega^2}\left[\int_0^{\infty}\frac{2\kappa}{\sqrt{\pi}}\epsilon^{-\kappa^2(\beta-\beta_0)^2}\,d\beta\right.$$

$$\left. - \int_0 \frac{2\kappa}{\sqrt{\pi}}\frac{\beta^2}{\omega^2}\epsilon^{-\kappa^2(\beta-\beta_0)^2}\,d\beta + \ldots\right]$$

$$\mathrm{R}(\omega) = \frac{1}{\pi}\frac{n}{\omega^2}\left[1 - \frac{\beta_0^2}{\omega^2}\left(1 + \frac{1}{\sqrt{\pi}}\frac{2}{\beta_0\kappa} + \frac{1}{2\kappa^2\beta_0^2}\right)\right.$$

$$\left. + \ldots\ldots \text{higher powers of } \left(\frac{\beta_0}{\omega}\right)\right].$$

Now in the case of our radio static we have for order of magnitudes:—

$$n = 1 \text{ to } 100,$$

$$\beta_0 = 10^3 \text{ sec.}^{-1},$$

$$\omega = \frac{2\pi}{\mathrm{T}} = \frac{2\pi(3\times 10^8)}{\lambda} \text{(metres, seconds).}$$

$$\therefore\quad \mathrm{R}(\omega) = \frac{1}{\pi}\frac{n\lambda^2}{\left[(2\pi)(3\times 10^8)\right]^2}$$

$$\times\left[1 + \ldots + \text{ terms of higher order in } \frac{\lambda}{(2\pi)(3\times 10^8)}\right].$$

It thus appears that, for static frequencies of the order of magnitude assumed, the energy distribution of static varies nearly as the square of the wave-length *.

The same conclusion follows with but slight modification in analysis for the previous assumption of square waves with a random frequency of occurrence, provided we let the average frequency of reversal approach the reciprocal of the average lengths of duration observed. The foregoing considerations lead us strongly to suspect that this property probably holds a considerable range of frequencies for most forms of impulsive physical discharges.

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* Provided ($\lambda < 100{,}000$ metres) and for a given width of frequency band $\Delta\omega$ (not a given $\Delta\lambda$). In terms of λ alone, since

$$|\,d\omega\,| = \left|\frac{(2\pi)(3\times 10^8)\,d\lambda}{\lambda^2}\right|$$

$$\mathrm{R}_{d\lambda}(\lambda) = \frac{1}{\pi}\frac{n}{(2\pi)(3\times 10^8)}.$$

7. *Summary and Conclusions.*

From the above analysis we see that the energy contained within a frequency band of given width due to a static produced by a random sequence of pulses of the forms investigated would vary directly with the square of the wave-length.

This result is in accord with Austin's early conclusions in the investigation of static on long waves[*], where he found the fields (proportional to the square roots of the energies) to vary roughly as the first power of the wave-length. The possibility of explaining the observed results from this point of view was qualitatively suggested by Pickard in a discussion of the paper[†].

From equation (31) we may investigate quantitatively the fraction of the energy due to the sequence of pulses in a given frequency band $\Delta\omega$. For simplicity we will confine ourselves to the exponential pulse case. The conclusions in all cases are essentially the same.

Note in this case

$$\text{Total Power} = \theta(\infty) = \operatorname*{Lim}_{T\to\infty} \frac{1}{T}\int_0^T [f(t)]^2 dt$$

$$= \frac{nT}{T}\int_0^\infty dt\, \epsilon^{-2\beta t}\int_{\beta=0}^{\beta=\infty} P(\beta)d\beta = n\int_{\beta=0}^{\beta=\infty}\frac{P(\beta)}{2\beta}d\beta$$

$$= \frac{n}{2}\left(\frac{1}{\beta}\right)_{\text{mean}} = \frac{n}{2}\frac{1}{\bar{\beta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\therefore \quad \frac{(R\omega)}{\theta(\infty)} = \frac{1}{\pi}\frac{2\bar{\beta}\lambda^2}{[2\pi(3\times10^8)]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Using the magnitude $\bar{\beta} = 10^3$ sec.$^{-1}$, this gives us something of the order of 10^{-4} as the total received *energy* of a static pulse of duration of the order of 10^{-3} second in a frequency width of 5000 cycles on 10,000 metres; at 1000 metres this fraction (varying with the square of the wave-length) has diminished to 10^{-6} and at 100 metres to 10^{-8}. It will be noted that, when the average duration of the pulse is long compared with the natural period of the signals in the given frequency band, halving the average duration of the pulses doubles the energy in the band, *provided* the root mean square value of the static remains constant, for this means the *number* of pulses must increase in direct proportion.

From the above analysis it appears that the energy due to gross outline of pulses of the order of 10^{-3} second in duration and square or sharply rising exponential form, can produce appreciable fields (proportional to the square roots of the energies) on the longer wave-lengths employed in practice, but that on the shorter waves pulses or ripples of smaller energy content but shorter duration will be increasingly important. Thus, as indicated by the square-wave investigation, a series of pulses of $\frac{1}{n}$ the energy content but n times the rate of reversal will produce the same high frequency energy. (See equation 22.)

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[*] Austin, L. W., "The Relation between Atmospheric Disturbances and Wave-Length in Radio Reception," Proc. I. R. E. ix. pp. 28-70 (February 1921).

[†] Pickard, G. W., Discussion on Austin's paper (*loc. cit.*), Proc. I. R. E. p. 36 (1921).

It will be noted that the methods employed in this paper are not confined in their application to the examples given (which are merely illustrations of the methods), but are useful in the harmonic analysis of many other types of irregular motions, such as voice waves, or noise.

APPENDIX A.

The final formula for $\theta(\omega)$ which we employ in our computations is as follows :—

$$\theta(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\sin \omega u}{u}\, du\left[\lim_{K \to \infty} \frac{1}{K-u}\int_0^{K-u} f(y)f(y+u)\, dy\right] \quad . \quad . \quad . \quad (1\,b)$$

(repeated)

In this formula it will be recalled that $f(y)$ is the function under analysis and K is the length of the interval. This formula for $\theta(\omega)$, which we employ, appears in somewhat generalized and modified form in Wiener's paper [*]. (See p. 121 ; Equation (47).)

Wiener obtains a function $R(f;\, u)$, which is, for the special case of well-behaved functions [†], exactly equal to twice our function $\theta(\omega)$.

$R(f;\, u)$ is given in his notation by the equation [‡]

$$R(f;\, u) = \frac{2}{\pi}\int_0^\infty \left\{\frac{3}{\pi}\lim_{h \to \infty} \int_{-\infty}^{\infty} \frac{\sin^4 ht}{t^4} f\left(t+\frac{\alpha}{2}\right)f\left(t-\frac{\alpha}{2}\right) dt\right\} \frac{\sin \alpha u}{u} d\alpha. \quad . \quad . \quad . \quad (A\,1)$$

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[*] Norbert Wiener, "The Quadratic Variation of a Function and its Fourier Coefficients," M. I. T. Bulletin, Dept. Math. Ser. 2, No. 75, March 1924.

[†] Norbert Wiener, "On the Representation of Functions by Trigonometrical Integrals," *Math. Zeitschrift*, Bd. 24, Heft 3, pp. 575–616 ; also M. I. T. Bulletin, Dept. Math. Ser. 2, No. 108.

[‡] Norbert Wiener, "The Harmonic Analysis of Irregular Motion," Journal of Math. and Physics, v. Nos. 2 and 3, February and March 1926.

In order to throw equation (A 1) into the form we shall use, however, we need several substitutions and changes of variable.

Wiener establishes, on p. 119 (Equation (44)), that

$$\int_0^\infty \cos 2\omega u\, d\{\mathrm{R}(f;u)\} = \frac{3}{\pi}\lim_{h\to 0}\frac{1}{h^3}\int_{-\infty}^{\infty}\frac{\sin^4 ht}{t^4}f(t+\omega)f(t-\omega)\,dt. \qquad \text{(A 2)}$$

Now if

$$\lim_{\mathrm{A}\to\infty}\frac{1}{2\mathrm{A}}\int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega)f(t-\omega)\,dt$$

exists, we have (p. 119 (1))

$$\tfrac{1}{2}\int_0^\infty \cos 2\omega u\, d\mathrm{R}(f;u) = \lim_{\mathrm{A}\to\infty}\frac{1}{2\mathrm{A}}\int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega)f(t-\omega)\,dt. \qquad \text{(A 3)}$$

Multiplying equation (A 3) by two and equating the right-hand member thus obtained to the right-hand member of equation (A 1) (Wiener's equation (44), p. 119 (12)), we have

$$\frac{3}{\pi}\lim_{h\to 0}\frac{1}{h^3}\int_{-\infty}^{\infty}\frac{\sin^4 ht}{t^4}f(t+\omega)f(t-\omega)\,dt$$
$$= 2\lim_{\mathrm{A}\to\infty}\frac{1}{2\mathrm{A}}\int_{-\mathrm{A}}^{\mathrm{A}} f(t+\omega)f(t-\omega)\,dt. \qquad \text{(A 4)}$$

Substituting equation (A 4) in equation (A 1) gives:—

$$\mathrm{R}(f;u) = \frac{2}{\pi}\int\frac{\sin\alpha u}{\alpha}\,d\alpha\left\{2\lim\frac{1}{2\mathrm{A}}\int_{-\mathrm{A}}^{\mathrm{A}} f\left(t+\frac{\alpha}{2}\right)f\left(t-\frac{\alpha}{2}\right)dt\right\}. \qquad \text{(A 5)}$$

Letting $t-\frac{\alpha}{2}=v$, and then altering variables of integration by letting $\alpha=u$ and $u=\omega$ in equation (A 5), gives, in the notation we have adopted,

$$\mathrm{R}(f;u) = \frac{2}{\pi}\int_0^\infty\frac{\sin\omega u}{u}\,du$$
$$\left\{2\lim_{\mathrm{A}\to\infty}\frac{1}{2\mathrm{A}}\int_{-\mathrm{A}-\frac{u}{2}}^{\mathrm{A}-\frac{u}{2}} f(v+u)f(v)\,dv\right\}. \qquad \text{(A 6)}$$

If, now, y is the distance from the left-hand end of our graph (*i.e.*, the smallest value of v for which our function is defined) and K the length of our interval, we have, in our notation,

$$\theta(\omega) = \frac{2}{\pi}\int_0^\infty\frac{\sin\omega u}{u}\,du\left\{\lim_{\mathrm{K}\to\infty}\frac{1}{\mathrm{K}-u}\int_0^{\mathrm{K}-u} f(y)f(y+u)\,dy.\right. \qquad \text{(A 7)}$$

XX. *Beryllium Spectrum in the Region* λ3367–1964. *By*

S. N. Bose, *Professor of Physics, Dacca University, and* S. K. Mukherjee, *Assistant Lecturer in Physics, Dacca University*[*].

[Plates II. & III.]

THE beryllium spectrum is remarkable owing to the small number of lines that have been observed in the visible and the ultra-violet. The earlier measurements are somewhat conflicting. Exner and Haschek could not find some of the lines observed by Rowland and Tatnall[†]. Glaser[‡] investigated the spectrum by sparking between the metal tips, but he also could not corroborate the earlier observations.

Recently Millikan and Bowen[§] subjected the spectrum to a thorough analysis by their method of hot spark, and extended it up to 1943 Å.U. They classified some of the important lines, and gave the term values both of Be II and Be I.

It was with a view to study the spectrum thoroughly, under different conditions of excitation, that the present work was undertaken.

The instrument that we have used almost exclusively for the work is Hilger's Quartz Spectrograph, type E 1. In the near ultra-violet between the regions 2400–1850 it is almost an ideal instrument for spectrum analysis, combining a high dispersion with a high light-value. We have extended our observations to the visible region; but here, because of the low dispersion, the measurements were not more accurate than by ·1 Å.U., though we could very easily identify the lines and thus verify the observations of the previous workers.

Most of the observations were made on the arc spectrum, and obtained by feeding the nitrate or the metal in a carbon arc. We have used both ordinary and Hilger's extra pure carbon rods, and the presence of traces of iron has been an advantage in furnishing suitable standard lines in the different regions. In the extreme ultra-violet we have used copper arc and spark as comparison spectra, and in some cases the silicon lines almost always present in carbon spectra were helpful in making accurate measurements.

The plates used were Ilford Empress and Ordinary up to 2175. In the extreme ultra-violet we tried sensitization with machine oil, but the lines were a little broad. As our aim was to resolve very narrow doublets, we could only get the best results by using Schumann plates as supplied by Hilger.

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[*] Communicated by the Authors.

[†] Kayser, *Handbuch d. Spectro.* vol. v.

[‡] Glaser, *Ann. d. Phys.* (4) lxviii. pp. 73–88 (1922).

[§] Millikan and Bowen, Phys. Rev., Aug. 1926.

The materials used were, at first, certain old samples of beryllium nitrate and metal from Merck's, which were found to contain lead, aluminium, and silver as impurities. Later, owing to the kindness of Professor Mark, of Badische Anilin Fabrik, we were enabled to get a different sample of the metal. But this was found to contain traces of rare earths, notably scandium and yttrium. By a comparison of the different samples the lines due to contamination were eliminated, and we give our results tabulated below (*vide* Table I.).

As may be seen, we could go almost to the same limit as Millikan and Bowen by their hot-spark method, and, incidentally, we have discovered that the following lines, 2351, 2175, 2126, 2056, and 2033, given as singlets by Millikan and Bowen, are clearly doublets of approximate wave-number difference 2·6. Most probably these are triplets due to the triplet P-terms, and our spectrograph could only separate P_1 from P_2+P_3. The wave-number difference thus measured is the distance of P_1 from the centre of gravity of P_2- and P_3-lines, and as such has a slightly higher value. The lines 1998 and 1964 just appeared as doublets, but owing to their hazy character the measurements of the doublet separation were not possible. We could verify the earlier measurements of Rowland and Tatnall as well as the line of Glaser, viz. λ 4672·9. Incidentally, we have discovered a few new lines whose wave-lengths are given in Table I. The line 3019 appeared as a doublet, the line 2986 as a triplet, and the lines 3110 and 2738 as singlets.

We have made some observations by feeding a fair amount of metal or the salt in the arc, and we could observe that the lines 3321, 2651, 2494, and 2175 with their components were reversed in some cases, thus showing that the *p*-level is probably the common origin of the lines as classified by Millikan and Bowen. In rare occasions, however, the line 3131, usually attributed to Be II, could be reversed. The line 2348 (1 S–2 P) is always reversed in the arc.

We have tried the spark spectra in air, where, owing to rapid oxidation, we could make very little progress. We have also tried sparking between the tips of the metal, enclosed in a partially evacuated vessel with quartz window; and even then we could not go beyond 2175. In this way, however, we have got an interesting band spectrum, which we believe to be due to beryllium and which consists of bands degraded to the red. The fine structures of the band have not yet been measured, and we give in Table II. the measurements of the edges.

There does not seem to be any line of Be between 4700 up to the extreme red. We are now continuing the work in the infra-red, and hope to be able to corroborate the solitary work of Theo Volk * in the region.

The following table gives the wave-lengths (in I. *a*, vac.) of the lines between λ 3367–1964, with the frequency difference between the components, and also the lines (in I. *a*) of Rowland and Tatnall, together with the few lines marked * observed by us as new :—

TABLE I.

Bose & Mukherjee.	Rowland & Tatnall. I. *a*.	Bowen & Millikan. I. *a*, vac.	δν.
3367·55	3367·579	—	-
*3110·91	-	—	—
*3019·54	—	—	—
*3019·33	—	—	—
2986·63	—	—	-
2986·44	2986·426	—	-
2986·08	2986·057	—	—
2898·26	2898·242	—	—
*2738·08	—	—	—
2351·40 }	-	2351·50	2·50
2351·54 }			
2175·72 }	-	2175·72	2·64
2175·84 }			
2126·30 }		2126·57	2·66
2126·42 }			
2056·65 }		2056·71	2·60
2056·77 }			
2033·23 }		2033·43	2·66
2033·34 }			
1998 (*a*)		1998·19	
(*a*)		1964·81	

The lines marked (*a*) appear in plates, but their measurements are unsatisfactory owing to the absence of standards in this region.

In the accompanying plates (Pls. II. and III.) I. and III. are contact-prints from Schumann plates; II. and IV. (*a*) are microphotographic enlargements for showing the fine structure; IV., contact-print from ordinary plate; V. and VI. are slightly enlarged prints to show the new lines.

The following table gives the wave-lengths (in I. *a*) of the edges of the band; those marked (*a*) are fully developed with their fine structures:—

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* Dissert. Tübingen, 1924 (Dresden bei Teubner). 17 pp.

TABLE II.

1	2474·2	6	2285·8
2 (*a*)	2446·0	7	2260·8
3 (*a*)	2419·2	8	2238·3
4 (*a*)	2325·1	9	2221·7
5 (*a*)	2299·4	10 (*a*)	2189·0

XXI. *Frequency Variations of the Triode Oscillator. A Reply to* Mr. D. F. MARTYN, *B.Sc., A.R.C.Sc. By* Lt.-Col. K. E. EDGEWORTH, *D.S.O., M.C., A.M.I.E.E.*[*]

IN the April number of the Philosophical Magazine there appeared a note of mine under the above title, in which I comment on a paper by Mr. D. F. Martyn (Phil. Mag., Nov. 1927), also with the same title. In my note I direct attention to a paper which I read before the Institution of Electrical Engineers (Wireless Section) on the 6th of January, 1926, and I remark: "So far as they cover the same ground, the experimental results appear to be in agreement, and the explanations offered are substantially the same. The main cause of frequency variations is associated with damping of one sort or another in the grid circuit, and, other things being equal, the magnitude of the frequency variation is proportional to the amount of damping. This type of frequency variation is referred to in my paper as a frequency variation of the first type."

In a further paper on the same subject (Phil. Mag., July 1928) Martyn rejects my statement, and it is necessary therefore that I should prove my words.

If a reference is made to my paper it will be found that seven different classes of circuit are dealt with:—

(i.) Tuned grid and tuned anode with normal coupling.
(ii.) Tuned grid and tuned anode with reversed coupling.
(iii.) Tuned grid and tuned anode with resistance coupling.
(iv.) Tuned grid and untuned anode with normal coupling.
(v.) Untuned grid and tuned anode with normal coupling.
(vi.) Tuned grid and untuned anode with reversed coupling.
(vii.) Untuned grid and tuned anode with reversed coupling.

No general solution is offered to cover all these different classes of circuit, but each class is dealt with separately.

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[*] Communicated by the Author.

Formulæ for frequency variations of the first type applicable to circuits of classes (i.) and (ii.) are given in equations (7), (8), (18), and (19) of my paper, attention being paid in each case to the appropriate sign.

The frequency variation of the first type is absent from resistance coupled circuits—Class (iii.).

A formula for the frequency variation of the first type applicable to circuits of class (iv.) is given in equation (20).

A formula for the frequency variation of the first type applicable to circuits of class (v.) is given near the end of my reply to the discussion.

Formulæ for the remaining two classes of circuit are not given, but can easily be obtained by the methods indicated in the paper.

Martyn tries to apply equation (8) to explain his experimental results, whereas this equation is obtained on the assumption that $L_1C_1 = L_2C_2$ and is clearly applicable to circuits of classes (i.) and (ii.) only.

The circuit used by Martyn in his experiments is a circuit with an untuned grid coil, and it belongs therefore to class (v). The equation given in my reply to the discussion is:

$$f=\frac{1}{2\pi\sqrt{L_1C_1}}\left\{1+\frac{1}{2A}\left(R_1-\frac{R_2C_2}{C_1}\right)-\frac{R_1R_2C_2}{2L_1}\right\}. \quad (A)$$

Where $R_2C_2 = R_4C_2 + L_2\sigma/G$: as explained in the note immediately following equation (18).

If R_4 (the resistance o. the grid coil) is neglected the equation reduces to

$$f=\frac{1}{2\pi\sqrt{L_1C_1}}\left\{1+\frac{1}{2A}\left(R_1-\frac{L_2\sigma}{C_1G}\right)-\frac{R_1L_2\sigma}{2L_1G}\right\}. \quad (B)$$

The equation is derived on the assumption that the variation is small compared with the natural frequency $1/\sqrt{L_1C_1}$.

Martyn's equation (8) is

$$p^2=\frac{1}{L_1C_1+k_1k_3(L_1L_2-M^2)}. \quad . \quad . \quad . \quad (C)$$

The equation is obtained on the assumption that the resistance of the anode coil is negligible.

The equations cover common ground when both assumptions are admissible.

Applying the second assumption to equation (B)—that is to say, putting $R_1 = 0$,—

$$f=\frac{1}{2\pi\sqrt{L_1C_1}}\left\{1-\frac{L_2\sigma}{2AC_1G}\right\}. \quad . \quad . \quad . \quad (D)$$

Applying the first assumption to equation (C)—that is to say, assuming that $k_1k_3(L_1L_2-M^2)$ is small compared with L_1C_1,—

$$p = \frac{1}{\sqrt{L_1C_1}}\left\{1-\frac{k_1k_3(L_1L_2-M^2)}{2L_1C_1}\right\}. \quad . \quad . \quad (E)$$

Observing that $\sigma = 1-M^2/L_1L_2$; $p = 2\pi f$; $A = 1/k_1$; $G = 1/k_3$, it is clear that equation (D) is identical with equation (E).

The identity of these two equations provides a formal proof that the frequency variation investigated by Martyn is the same as the frequency variation of the first type discussed in my paper, and justifies the statement in my previous note which is quoted at the head of this paper.

Most of the points discussed in Martyn's first paper—the significance of the quantity $k_1k_3(L_1L_2-M^2)/L_1C_1$ or $L_2\sigma/(AGC_1)$, the conditions of minimum variation, and so on—can be derived from any of the above equations with equal facility.

The following quotations are also significant :—Martyn, "The most important cause of frequency variations is found to be the flow of grid current" ; Edgeworth, "The damping in the grid circuit is of fundamental importance, since it determines the whole scale on which the frequency variations occur."

I should now like to offer some comments on the latter part of Martyn's second paper, in which he describes in some detail his efforts to reduce the frequency variations to a minimum. He claims that "the frequency remained constant to one part in 100,000, *even when the filament current was deliberately varied*, . . ." (Martyn's italics). I wish to state that results of precisely the same order were demonstrated to me by the engineers of the Marconi Company early in 1925. I believe that a grid leak of 2 or 3 megohms was used in conjunction with the usual grid leak condenser.

The results of my own experiments, which were carried out shortly after the above demonstration, are shown in fig. 22 of my paper. The filament voltage was varied from 3·8 to 4·2, and the resulting frequency variations were :—

With no grid leak	1 in 1,000
With a grid leak of ·02......	1 in 2,500
With a grid leak of ·1	1 in 12,000
With a grid leak of ·5	1 in 40,000

The use of larger grid leaks is not mentioned, but it is surely evident that the use of a larger grid leak would reduce the frequency variation still further.

As a matter of fact not very much use has been made of these results. The main difficulty about the valve oscillator as a standard of frequency is that it is very difficult to keep the capacity of the circuit constant under ordinary working conditions, more especially if the oscillator is required to drive another valve circuit.

For this reason the valve driven tuning-fork and the valve oscillator with crystal control seem to have captured most of the field. The results obtainable by these methods are constantly referred to in current wireless periodicals, and need not be described in detail here.

XXII. *The Raman Spectra of Scattered Radiation.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In the October number of the Philosophical Magazine (1928) Prof. R. W. Wood gives important new data confirming the discovery of Raman that the frequency difference between the companion line and the exciting line is constant and equal to the frequency of an infra-red absorption band. Since his calculated infra-red absorption bands of calcite lack comparative data based upon direct observations, the following tabulations may be of interest:—

Benzol.— Calculated from scattered radiation		Observed by Coblentz.	
Raman.	Wood.		
3·27 μ	3·27 μ	3·25 μ	
6·28	6·23 & 6·30	6·25	Complex.
8·57	8·55	8·67 (8·5 to 8·7)	Complex.
10·10 10·13	10·05 10·15	10·0 to 10·3	Complex.
11·78	11·78	11·8	
Calcite.—	5·78	5·8	Complex.
	9·19	9·2	
	14·	14·1	(Obs. by Nyswander).

The direct observations on calcite are taken from papers by Coblentz and by Nyswander; those on benzol were obtained by Coblentz. Owing to the small dispersion, the absorption bands of calcite at 5·8 μ and 9·2 μ, also of benzol at 6·25 μ, 8·6 μ, and 10·2 μ, are not completely resolved. Taking this into consideration, the agreement between the calculated and the observed values is as good as can be expected until we can obtain new infra-red measurements.

Bureau of Standards,
Washington, D.C.
October 29, 1928.

Respectfully submitted,
W. W. COBLENTZ.

XXIII. *On the Intensity of the Scattered Light from an Unpolarized Beam.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

RAYLEIGH gives in his original memoir on light-scattering from small particles (Phil. Mag. xli. p. 113, 1871) the following expression for the intensity of scattered light from a volume element containing *m* particles when the primary beam is unpolarized:

$$A^2\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{mT^2}{\lambda^4 r^2}.$$

where A^2 is the intensity in the primary beam. Rayleigh points out later that a factor π^2 was omitted and the expression should be

$$A^2\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{mT^2\pi^2}{\lambda^4 r^2}.$$

By integrating over a sphere the coefficient of attenuation of the primary beam is obtained in the form

$$h=\frac{16}{3}\pi^3\frac{mT^2}{\lambda^4}\frac{(D'-D)^2}{D^2}, \quad (I=I_0e^{-hr}),$$

where *m* is now the number of particles per unit volume of the turbid medium. This differs from the result derived by Rayleigh (Phil. Mag. xlviii. p. 377, 1899) for a polarized beam, namely

$$h=\frac{8\pi^3}{3}\frac{mT^2}{\lambda^4}\frac{(D'-D)^2}{D^2}$$

by the factor 2. The coefficient of attenuation for polarized and unpolarized beams must, however, be the same. On checking the integration leading to the expression (1), it appears that Rayleigh has inadvertently omitted a factor of $\frac{1}{2}$, and (1) should run

$$\frac{A^2}{2}\frac{(D'-D)^2}{D^2}(1+\cos^2\beta)\frac{m\mathrm{T}^2\pi^2}{\lambda^4 r^2}.$$

Rayleigh bases none of his later work on formula (1), so that the error is not propagated. Other writers have used the result, however, and it may be useful to draw attention to the amendment necessary.

The unamended result is reprinted in Rayleigh's 'Collected Works,' Wood's 'Physical Optics,' and other standard works.

Yours faithfully,
W. S. Stiles.

XXIV. *The Constant of Mass Action.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In a recent communication (Phil. Mag. ser. 7, v. p. 263, 1928) R. D. Kleeman develops an expression for the Constant of Mass Action differing in a fundamental particular from the van't Hoff equation.

In his equation (6) (*loc. cit.* p. 267),

$$\begin{aligned}\mathrm{RT}\ln\frac{(p_C'')^c(p_D'')^d}{(p_A'')^a(p_B'')^b}&=\mathrm{RT}\ln\frac{(p_C')^c(p_D')^d}{(p_A')^a(p_B')^b}\\&+\Big[c\mathrm{RT}\ln C'+c\Sigma\frac{-C_n}{(n-1)(C'p_C')^{n-1}}\\&-c\mathrm{RT}\ln C''-c\Sigma\frac{-C_n}{(n-1)(C''p_C'')^{n-1}}\\&+d\mathrm{RT}\ln D'+d\Sigma\frac{-D_n}{(n-1)(D'p_D')^{n-1}}\\&-d\mathrm{RT}\ln D''-d\Sigma\frac{-D_n}{(n-1)(D''p_D'')^{n-1}}\Big],\end{aligned}$$

the factor in the square brackets has been obtained on the assumption that in the removal of the "sepro-unstable" molecules, C and D, from the equilibrium box, they dissociate into their equilibrium mixture, so that the pressures between which they are compressed are not p_C'', p_C', p_D'', p_D', as van't Hoff supposed, but terms depending on the degree of dissociation.

I would point out that Kleeman has not considered the free energy decrease in the dissociation of these "sepro-unstable" molecules on removal from reservoir II., from the pressures p_C'', p_D'', to the equilibrium mixtures at the pressures $C''p_C''$, $D''p_D''$, and the free energy increase required to convert the equilibrium mixtures at pressures $C'p_C'$, $D'p_D'$, to the "sepro-unstable" molecules at pressures p_C', p_D', on return to reservior I. These free energy terms are not equivalent, and if they are considered it can be shown very simply by the usual methods of thermodynamics that the free energy increase in transferring c molecules of C from a pressure p_C'' to a pressure p_C' is $c\mathrm{RT}\ln\frac{p_C'}{p_C''}$, and that the similar term for D is $d\mathrm{RT}\ln\frac{p_D'}{p_D''}$. The Constant of Mass Action then reduces to the simple van't Hoff form. It may be emphasized here that the free energy change in any alteration of a system between given states is independent of the path chosen, provided that every process in the path is carried out under isothermal and reversible conditions.

In the conclusion of his paper Kleeman puts forward kinetic evidence in support of his new Constant of Mass Action which is substantially the kinetic theory proof of the Law of Mass Action in terms of activities (compare H. S. Taylor, 'Treatise on Physical Chemistry' (1924), vol. i. p. 299). Kleeman's factor κ is not a correction for the velocity of reaction k, but is the activity coefficient of the concentration term.

Yours faithfully,

R. F. Goldstein.

Crumpsall, Manchester.
Sept. 29th, 1928.

XXV. *The Constant of Mass Action.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

MR. GOLDSTEIN, in his criticism of my paper on the Constant of Mass Action in the preceding letter to this Journal, states that the changes in free energy on removing dissociating molecules from the reservoirs of a van't Hoff cycle do not vanish, and that if these changes are taken into account van't Hoff's result is obtained. He does not, however, show how this is done. May I point out that in the van't Hoff cycle it is usually supposed that the conditions are such that no change in the partial pressure of the kind of molecules in a reservoir takes place of which a small fraction is removed, which will then also hold for the pressure in the cylinder used for removing them independently of dissociation, in which case the change in free energy is zero, since $\partial p=0$. The removed molecules will tend to be replaced by a resultant association or dissociation taking place in the mixture, depending on whether or no these molecules dissociate after removal. I may add that we may assist, if we like, in maintaining the partial pressures constant by means of various agents and conditions; thus, for example, we may suppose that a part of the reservoir contains a substance which occludes in part the gaseous mixture etc.

This letter gives me an opportunity to point out that the result I have obtained may be deduced more simply by equating to zero the external work done during the cycle (or equating the work along two different paths) instead of the change in free energy. Referring to my paper (Phil. Mag. v. p. 263, 1928), this gives

$$
\begin{aligned}
a\mathrm{RT}+b\mathrm{RT}+a\int_{p_{A'}}^{p_{A''}} p\cdot\frac{\partial r}{\partial p}\cdot\partial p+b\int_{p_{B'}}^{p_{B''}} p\cdot\frac{\partial r}{\partial p}\cdot\partial p-a\mathrm{RT}-b\mathrm{RT}&\\
=c\mathrm{C}'p_{\mathrm{C}}'r_{\mathrm{C}}'+d\mathrm{D}'p_{\mathrm{D}}'r_{\mathrm{D}}'+c\int_{\mathrm{C}'p_{\mathrm{C}'}}^{\mathrm{C}''p_{\mathrm{C}''}} p\cdot\frac{\partial r}{\partial p}\cdot\partial p&\\
+d\int_{\mathrm{D}'p_{\mathrm{D}'}}^{\mathrm{D}''p_{\mathrm{D}''}} p\cdot\frac{\partial r}{\partial p}\cdot\partial p-c\mathrm{C}''p_{\mathrm{C}}''r_{\mathrm{C}}''-d\mathrm{D}''p_{\mathrm{D}}''r_{\mathrm{D}}'',&\quad\ldots\quad(1)
\end{aligned}
$$

where r_{C}' and r_{C}'' denote the volumes of a molecule C in a partly dissociated state after removal from the reservoirs I. and II. respectively, and r_{D}' and r_{D}'' have similar meanings in respect to a molecule D. These volumes are obtained from the equations

$$r_{\mathrm{C}}=\frac{\mathrm{RT}}{p}+\Sigma\frac{\mathrm{C}_n}{p^n}, \quad\ldots\ldots\quad (2)$$

$$r_{\mathrm{D}}=\frac{\mathrm{RT}}{p}+\Sigma\frac{\mathrm{D}_n}{p^n}, \quad\ldots\ldots\quad (3)$$

which correspond to the general equation (4) given in the paper quoted. If equation (1) is transformed by means of equations (2) and (3) and the gas equations given in the paper, it assumes the form

$$\mathrm{RT}\ln\frac{(p_{\mathrm{C}}'')^{c}(p_{\mathrm{D}}'')^{d}}{(p_{\mathrm{A}}'')^{a}(p_{\mathrm{B}}'')^{b}}=\mathrm{RT}\ln\frac{(p_{\mathrm{C}}')^{c}(p_{\mathrm{D}}')^{d}}{(p_{\mathrm{A}}')^{a}(p_{\mathrm{B}}')^{b}}+\mathrm{X}, \quad . \quad (4)$$

where X is a quantity which vanishes only if the molecules C and D do not dissociate when removed from the reservoirs I. and II. It can then be shown, in exactly the same way as before, that the constant of mass action may be a function of the volume and masses of the interacting constituents as well as of the temperature.

The statement made by Mr. Goldstein that the quantity κ I have introduced is nothing else than the activity coefficient of the concentration term is entirely erroneous, as can best be shown by considering a concrete example. The constant of mass action of a gaseous reaction between the molecules ce, c_2, and e_2 in terms of the corresponding molecular activities a_{ce}, a_{c_2}, a_{e_2} is $(a_{ce})^2/a_{c_2}a_{e_2}$, while the expression involving the κ's is $k_1\kappa_1/k_2\kappa_2$, where k_1 expresses the chance of a molecule ce encountering another molecule ce, and κ_1 the chance of two molecules c_2 and e_2 being formed on account of an encounter, and k_2 and κ_2 have similar meanings. Obviously the κ's are not identical with the a's; in fact κ is a new and important quantity which is intimately associated with the functional nature of the constant of mass-action, which is a function of the temperature only when the gas equation holds and $\kappa_1=\kappa_2$.

Yours faithfully,
R. D. KLEEMAN.

Schenectady, N.Y., U.S.A.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

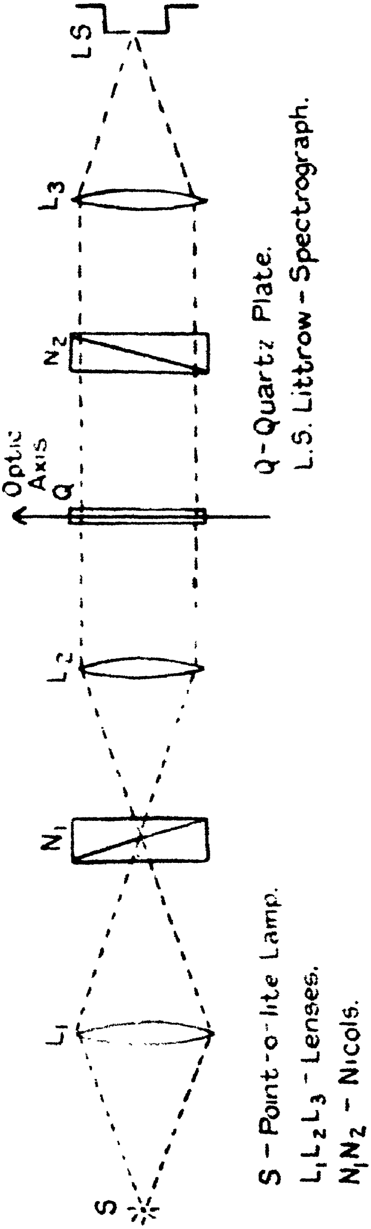

S
L_1
N_1
L_2
Q
Optic Axis
N_2
L_3
LS
S – Point-o-lite Lamp.
$L_1L_2L_3$ – Lenses.
N_1N_2 – Nicols.
Q – Quartz Plate.
L.S. Littrow – Spectrograph.

FIG. 1.

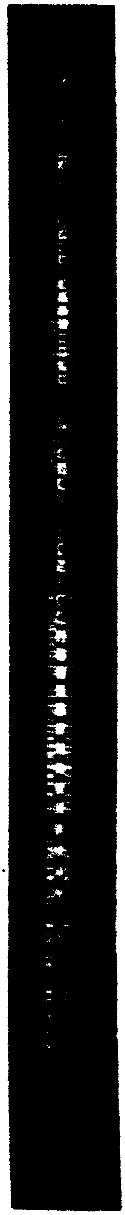
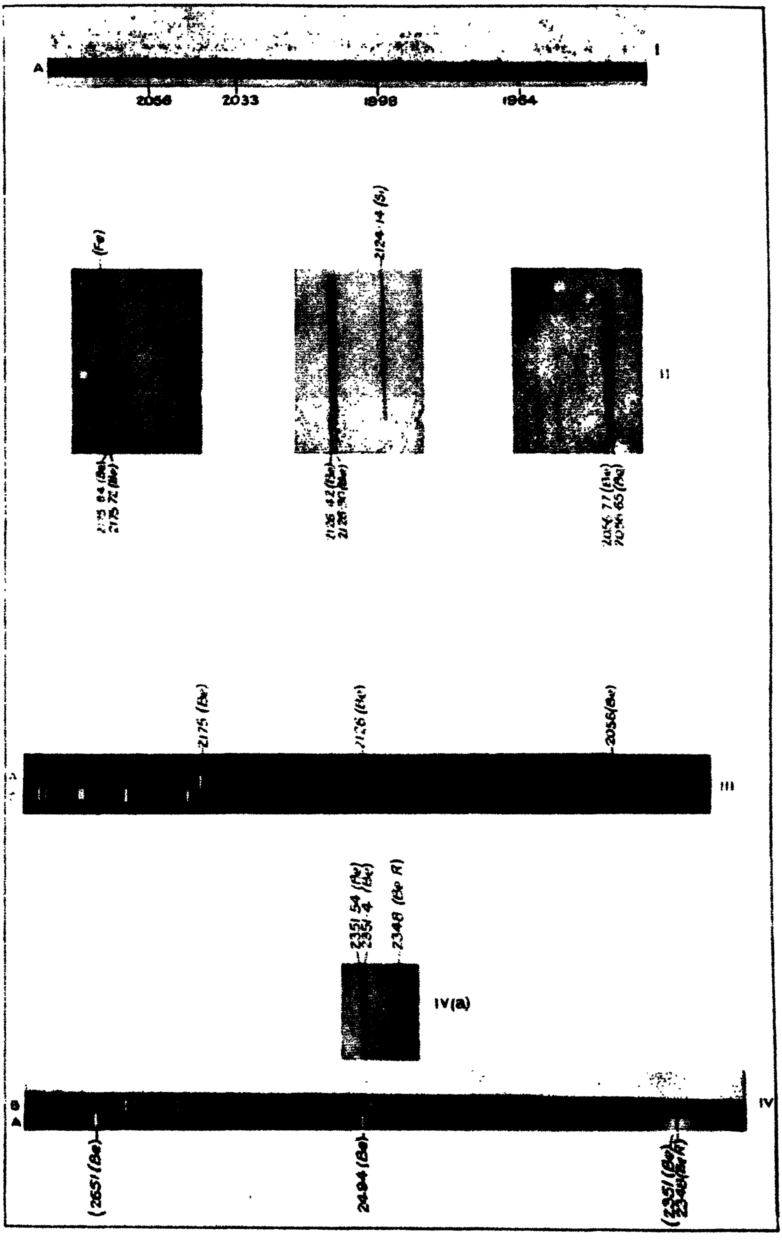
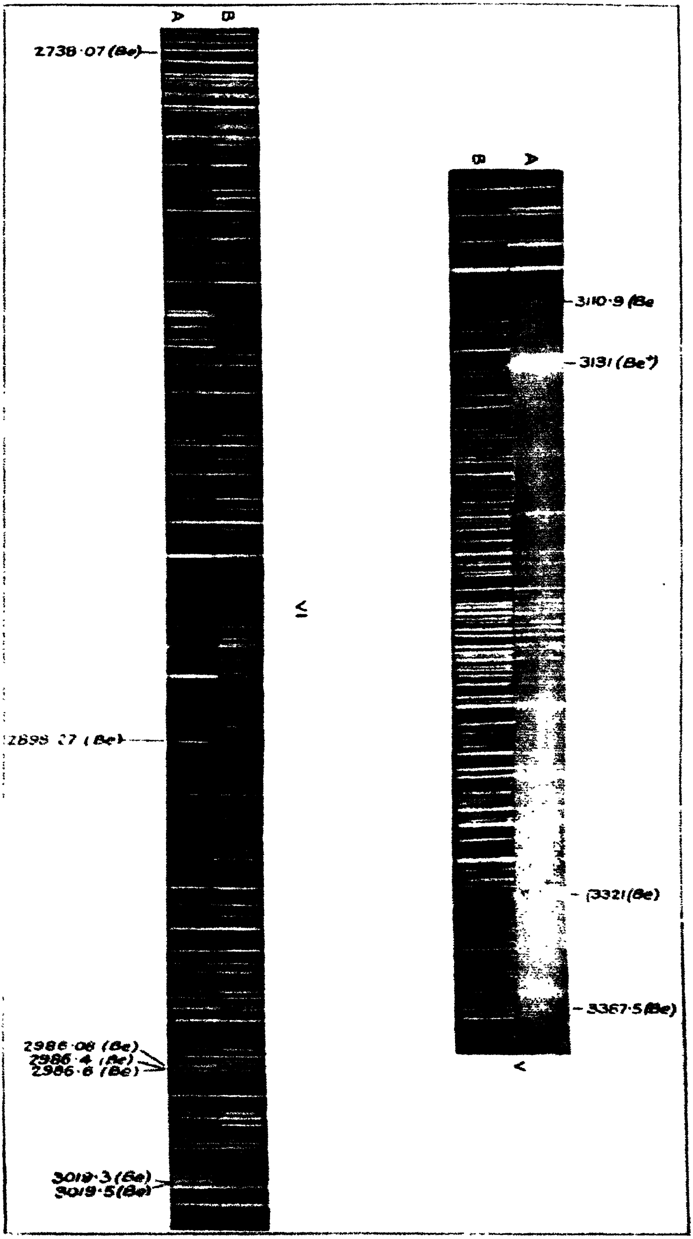


FIG. 2.



A. Carbon arc fed with Be Salt.
B. Iron arc.
C. Copper arc.



A. Carbon arc fed with Be Salts.
B. Iron Arc.

THE
LONDON EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

FEBRUARY 1929.

XXVI. *The Heats of Solution of some Salts in Water and Ethyl Alcohol Solutions.* *By* Prof. J. R. PARTINGTON *and* Dr. W. E. SOPER *.

Introduction.

THE increasing interest which is now being shown in solutions of electrolytes in non-aqueous media led to the somewhat surprising discovery that there are practically no data for the heats of solution and dilution in such media. This work is a preliminary attempt to fill this gap to some degree, and, for this reason, it has been thought to be of more advantage to examine the salts chosen at each end of the concentration range, rather than to examine the whole concentration range, the middle portion of which is relatively unimportant from a theoretical standpoint. The heats of solution and dilution of the same salts in water do not appear to have been recorded completely at the points chosen, and have therefore been included for purposes of comparison. The heats of solution and dilution of potassium chloride in water have been included as a check on the experimental method.

One of the authors (W. E. S.) is indebted to the Chemical Society and to the Dixon Fund of the University of London for grants towards the purchase of apparatus and materials. The work is part of a thesis submitted by W. E. Soper for the degree of Ph.D. of the University of London.

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* Communicated by the Authors.

Definition of the various Heats of Solution and Dilution.

The *integral heat of solution* for concentration c, denoted L_c, is the heat evolved by the solution of one mol of a substance in as much pure solvent as is required to make a solution of concentration c. In the special case when $c=0$, $L_c=L_0$, the *first heat of solution*, and when c corresponds with saturation, $c=s$, L_c is equal to the *total heat of solution*, L^s. The integral heat of a solution in which m mols of solute are dissolved in a mols of solvent is denoted by the symbol ${}_aL^m$, where $m/a=c$. The *intermediate heat of solution* is the heat evolved by the solution of solute in an already prepared solution. If we dissolve one mol of a solute in an infinitely large quantity of solution of concentration c, so that the concentration of the solution is practically unaltered, then we have the *true intermediate* or *differential heat of solution*, Λ_c. In the special case when $c=s$ we have the theoretically important *final heat of solution*, Λ_s. This is sometimes called the "theoretical" or "fictitious" heat of solution. In a practical case n mols of solute are dissolved in a solution already containing m mols of solute in a mols of solvent, so that a measurable change in concentration takes place. This quantity is denoted the *intermediate heat of solution* ${}^m_a\Lambda^n$. The heat of solution calculated from this is the *mean intermediate heat of solution*, Λ_c', which can be obtained from the mean concentration c of the concentrations before and after the addition of the solute. The differential heat of solution corresponds with the *differential heat of dilution*, ϕ_c, which is the quantity of heat evolved on addition of one mol of solvent to an infinite quantity of a solution of concentration c, so that practically no change in concentration takes place. In the case of a saturated solution, the magnitude here involved is given the name, *first heat of dilution*, ϕ_s. In a practical case one dilutes a solution containing m mols of solute in a mols of solvent with a large quantity of solvent, b mols. The heat of reaction involved is called the intermediate heat of dilution, ${}^m_a\phi_b$. From first principles it is seen that there exist certain simple relations between the various heats of solution and dilution, and from some of these relations we obtain results from indirect calorimetric determinations. We have first relations:—

$$ {}_aL^m + {}^m_a\Lambda^n = {}_aL^{m+n} \quad \ldots\ldots \quad (1) $$

$$ {}_aL^m + {}^m_a\phi_b = {}_{a+b}L^m \quad \ldots\ldots \quad (2) $$

If we start out with a solution containing m mols of solute in a mols of solvent, and add n mols of solute, we have the intermediate heat of solution evolved, ${}^{m}_{a}\Lambda^{n}$. If, now, we dilute this solution with b mols of solvent, and in so doing we bring the solution back to the original concentration, *i. e.*, $m/a = n/b$, we obtain the intermediate heat of dilution, ${}^{m+n}_{a}\phi_{b}$, and the following relation holds :—

$$ {}^{m}_{a}\Lambda^{n} + {}^{m+n}_{a}\phi_{b} = {}_{b}\mathrm{L}^{n}. \quad . \quad . \quad . \quad . \quad . \quad (3) $$

If the concentration is given in molar fractions, then we may generalize from equation (3), and obtain

$$ \mathrm{L}_{c} = \Lambda_{c} + 1/c \, . \, \phi_{c}. \quad . \quad . \quad . \quad . \quad . \quad (4) $$

In the present work the following calorimetric determinations have been made in order to arrive at the various heats of solution and dilution. Single portions of solute have been introduced successively into a fixed quantity of solvent, and a series of mean intermediate heats of solution calculated for one mol of solute at the mean concentration of each interval. In this way the differential heat of solution is obtained, a correction for curvature being applied where necessary, on the basis of the mean value equation :—

$$ \Lambda'_{c} = \frac{{}^{m}_{a}\Lambda^{n}}{n} = \int_{ma}^{(m+n)a} \Lambda_{c} \, dn. $$

The remaining values were then obtained by use of the formulæ just given. In the neighbourhood of saturation, however, this method fails, because here the process of solution takes too long a time. In this region, especially for the determination of the total heat of solution and the final heat of solution, a different method was used. A concentrated initial solution was diluted one or more times with solvent, and the heats of dilution evolved were measured. With each of these was combined the known integral heat of solution by means of formula (2), and the other unknowns were thus calculated.

Previous Measurements.

The classic investigations of Julius Thomsen were begun in 1853. A large number of salts were investigated, but the measurements were as a rule limited to one concentration, and to water as a solvent.

Berthelot commenced his equally famous investigations in 1865, and investigated several salts. His measurements also were generally confined to one concentration.

In 1888, S. U. Pickering[1] published the results of a series of investigations of the heats of solution of certain salts in water and in anhydrous ethyl alcohol. He obtained the following results among others :—

TABLE I.

Salt.	Weight of salt used, grams.	Weight of solvent, grams.	Heat of solution, g. cals./mol salt.
Earlier determinations.			
$Ca(NO_3)_2$	1·006	214·39 (EtOH)	7548
$Ca(NO_3)_2 . 4H_2O$......	2·855	214·39 (EtOH)	1835
Later determinations.			
$Ca(NO_3)_2$	2·3312	476·76 (EtOH)	8708
$Ca(NO_3)_2$	2·2419	476·76 (EtOH)	8711
$Ca(NO_3)_2$	14·687	400·00 (H_2O)	3940
$Ca(NO_3)_2$	14·842	400·00 (H_2O)	3945
$Ca(NO_3)_2 . 4H_2O$......	20·803	400·00 (H_2O)	−8354
$Ca(NO_3)_2 . 4H_2O$......	19·796	400·00 (H_2O)	−8354

In the earlier experiments an open calorimeter was used, but in the later experiments the calorimeter was made larger and fitted with a lid.

Von Steinwehr[2] in 1901 introduced the method of differential calorimetry to measure the heat of dilution of hydrochloric acid. He measured temperature differences by means of thermocouples.

In 1905, Richards, Henderson, and Forbes[3] first introduced the practice of adiabatic calorimetry. Hot water was first used to maintain the adiabatic condition of the outer bath, but this was afterwards replaced by the heat of neutralization of alkali by acid. This method was improved by Richards, Henderson, and Frevert[4] for use in the determination of heats of combustion. Richards and Rowe[5] in 1908 used the method for the determination of the specific heats of liquids, when heat was supplied to the liquid in the calorimeter by immersion of a platinum vessel in which acid and alkali were mixed. This was further elaborated by Richards and Rowe in 1920 and 1921[6] for the determination of heats of dilution.

Rümelin[7] in 1907 measured among others the heat of dilution of various solutions of calcium nitrate in water. He used a double calorimeter and measured the difference in temperature of the two vessels by means of thermocouples.

The temperature at which the experiments were performed, however, varied between 17° and 20° C.

In comparing the effects of various non-aqueous solvents, Walden(8) measured the heats of solution of potassium iodide, tetraethylammonium iodide, and tetrapropylammonium iodide in a variety of solvents. Some of his results will be tabulated for comparison purposes.

TABLE II.

Weight of salt, grams.	Weight of solvent, grams.	Molecular proportions.	Temp. rise.	Integral heat of solution, g. cals./mol salt.	
Potassium Iodide in Water at 18° C.					
5·145	111·60	1 : 200	−1·265	−5145	
5·270	114·17	1 : 200	−1·270	−5156	
Potassium Iodide in Methyl Alcohol at 18° C.					
2·105	81·26	1 : 200	−0·160	− 752	
Potassium Iodide in Ethyl Alcohol at 18° C.					
1·4452	80·22	1 : 200	−0·340	−2204	Mean.
1·147	86·9	1 : 273	−0·230	−2124	−2140
1·105	86·9	1 : 284	−0·225	−2156	
0·7206	79·98	1 : 400	−0·167	−1994	
0·533	86·78	1 : 586	−0·080	−1521	−1537
0·496	84·10	1 : 612	−0·075	−1552	
Potassium Iodide in Acetone at 18° C.					
1·400	87·70	1 : 179	0·580	4050	4079
1·391	86·60	1 : 178	0·590	4108	
1·076	75·34	1 : 200	0·553	4153	4188
1·132	79·23	1 : 200	0·568	4223	
0·600	86·95	1 : 411	0·275	4420	

De Kollosowski(9) has measured a series of heats of solution of various salts at various concentrations in aqueous ethyl alcohol as solvent.

Various designs of adiabatic calorimeters have since been described for the measurement of heats of solution, among which are these of Wust and Lange(10) and Lange and Schwartz(11). Cohen, Moesveld, and Helderman(12) describe a calorimeter in which electrical energy is passed into a solution which is being cooled by a negative heat of solution, and thus the temperature of the mixture remains practically constant. No further record of any measurements with anhydrous ethyl alcohol has been found.

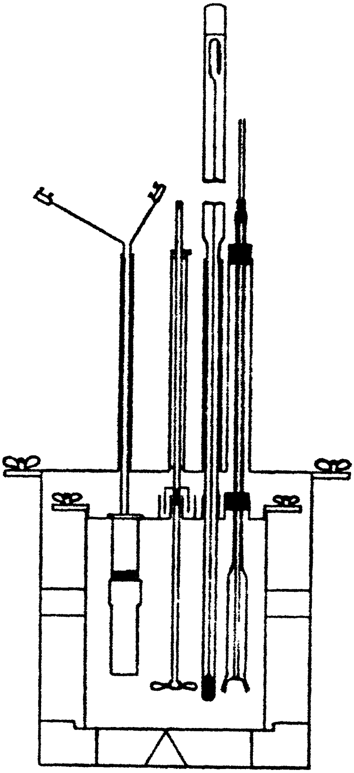
References.

(1) S. U. Pickering, J. C. S. liii. p. 865 (1888).
(2) Von Steinwehr, *Zeit. physik. Chem.* xxxviii. p. 185 (1901).
(3) Richards, Henderson, and Forbes, *Zeit. physik. Chem.* lii. p. 551 (1905).
(4) Richards, Henderson, and Frevert, *Zeit. physik. Chem.* lxix. p. 532 (1907).
(5) Richards and Rowe, *Zeit. physik. Chem.* lxiv. p. 187 (1908).
(6) Richards and Rowe, J. A. C. S. xlii. p. 1621 (1920); xliii. p. 770 (1921).
(7) Rümelin, *Zeit. physik. Chem.* lviii. p. 449 (1907).
(8) Walden, *Zeits. physik. Chem.* lxix. p. 192 (1908).
(9) De Kollosowski, Bull. Acad. Roy. Belg. 1912, p. 591, 1913, pp. 36, 329; *Journ. Chim. Phys.* xxii. p. 97 (1925).
(10) Wust and Lange, *Zeit. physik. Chem.* cxvi. p. 161 (1925).
(11) Lange and Schwartz, *Zeit. physik. Chem.* cxxxiii. p. 129 (1928).
(12) Cohen, Moesveld, and Helderman, *Zeit. physik. Chem.* xcv. p. 317 (1920).

The Experimental Method.

The calorimeter employed (fig. 1) could be used either isothermally or adiabatically. The calorimeter vessel, made of spun copper and silver-plated, was enclosed in a submarine jacket made of sheet-copper. It was supported inside the jacket by cork wedges which served for thermal insulation. The calorimeter was fitted with a brass lid to prevent evaporation of the liquid into the air-space between it and the jacket. The liquid in the calorimeter was stirred by an ordinary propeller stirrer of copper heavily silver-plated. The propeller shaft ran in bearings which were attached to the submarine jacket, and it was at the same time supported by it. In this way the stirrer was free from contact with the calorimeter, and heating by friction was avoided. Evaporation from the calorimeter through the entrance of the stirrer was prevented by fitting an annular oil-seal to the top of the calorimeter lid and to the propeller shaft. Heat conduction along the propeller shaft, which was made from silver-plated copper inside the calorimeter and from brass from the annular seal upwards, was avoided by interposing a short shaft of ebonite at the junction between the silver-plated shaft and the oil-seal on the top of the calorimeter. The resistance heater was made to screw into an "Ivoride" cylinder which was clamped to the calorimeter lid. The heater was connected in series to a battery of accumulators by heavy copper wires, and the current passing through the heater was measured by measuring the fall in potential across a standard 1-ohm resistance which was connected in series in the circuit. The temperatures of the calorimeter liquid and of the outer bath were measured by calibrated Beckmann thermometers.

Fig. 1.



This is a brief outline of the experimental arrangement, several details of which will now be described more fully.

The Calorimeter and Lid.

The calorimeter consisted of a spun-copper beaker of 550 c.c. content, the rim of which was removed and replaced by a flange with five bolts projecting from it. The inside of the calorimeter was heavily silver-plated, and except in two cases, when the solution was a concentrated aqueous solution of a halide ($CuCl_2$ and KCl), this was sufficient to protect the copper. In these other cases, provided that the concentrated solution was not left for too long a time in the vessel, it wâs found sufficient to cover the silver with a thin film of vaseline in order to protect it. The lid of the calorimeter fitted over the five bolts projecting from the flange and was fastened by means of wing nuts. An indiarubber washer was placed between the calorimeter flange and lid. The central part of the lid was sunk into the calorimeter for a short distance in order that it could be in thermal contact with the sides of the calorimeter in spite of the indiarubber washer, and thus prevent, as far as possible, condensation on the lid.

The lid was provided with holes fitted with chimney-like projecting tubes about three-quarters of an inch long for the introduction of a pipette, a thermometer, and the stirrer (this latter having an annular seal). The thermometer was steadied by a sleeve over itself and the projecting copper tube. The resistance heater was threaded on to a cylinder of "Ivoride," about one and a half inches long, which was clamped to the lid.

The Calorimeter Heater.

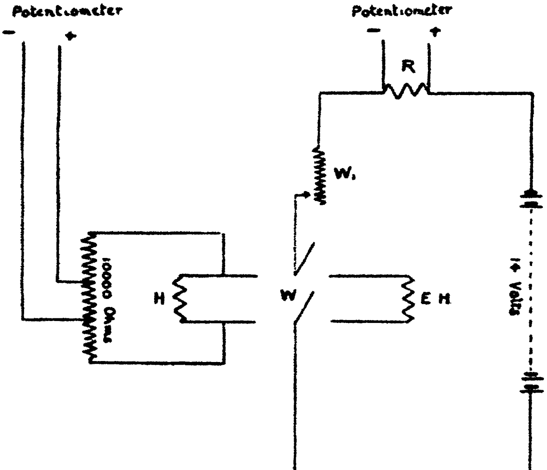
The development of a satisfactory heater was a somewhat difficult problem. The resistance wire must be insulated from the solution, and the insulation must be impervious to the latter. The final arrangement adopted was as follows:—About 4 feet of 30 S.W.G. nickel chrome wire was wound into a spiral which was pulled out to the required length and wound round a former consisting of a flat piece of "Micanite" with a saw edge cut on each side. The wire was supported by this in such a way that it was not in contact with the "Micanite" except at the saw edges. The lead from the bottom of the spiral was insulated with an asbestos sleeve and brought up through the middle of the spiral. The leads were pinched into two small brass terminals which were brought through the lid of a cylindrical copper case and insulated from it by two ebonite bushes. The heavy copper leads were soldered into the top caps of the terminals. The heating coil was then put into the cylindrical copper vessel, the spiral being allowed to press against the side, but insulated from it by a single sheet of "Micanite." The lid and vessel were then soldered together, the whole being copper-plated and then heavily silver-plated.

The Energy Measurement.

The electrical energy supplied to the calorimeter heater was determined by measuring the potential drop across the ends of the heater windings and the potential drop across a standard 1-ohm resistance which was in series in the circuit. The arrangement used is shown in the diagram (fig. 2).

H is the heater through which the current flowed from the battery B through one-half of the closed double-throw switch W. The regulating resistance W_1 consisted of two slide rheostats. R was the standard 1-ohm resistance. In parallel with the heater windings was an accurately-known resistance of 10,000 ohms, and from this a resistance of 1000 ohms was tapped off to give 1/10 of the total fall of potential across the 10,000 ohms, and therefore across the heater windings. This fall in potential and also the fall in potential across the standard 1-ohm resistance was measured on a special Tinsley ionization potentiometer against a standard Weston cell. The current was not switched directly on to the heater in the course of an experiment, but was previously switched on through the resistance coil E.H., equal in resistance to the calorimeter heater, by means of the other half of the double-throw switch W. By this

Fig. 2.



means the accumulators were allowed to settle down to a more or less steady potential, and this was not upset on quickly switching over to the heater.

The measurement of the time of heating was made by a carefully-regulated stop-watch, which could be read accurately to one-twentieth of a second.

For the conversion of electrical energy into heat the value

$$1 \text{ joule} = 0{\cdot}2389 \text{ calorie}$$

was used.

The Submarine Jacket and the Outer Bath.

The submarine jacket of sheet copper provided a 1-inch air-gap. It was fitted at the top with a flange carrying six bolts, on to which the lid was clamped with a thick india-rubber washer. The lid was provided with tubes 7 inches long for the introduction of the pipette and thermometer, and for bringing out the heater leads, which were insulated from each other and from the case by sleeving of "Sistoflex" reaching down to the top of the heater.

The tube for the stirrer shaft was fitted with brass bushes at the top and the bottom, and the shaft was supported on the top bush by a collar. The calorimeter stirrer was driven by a small electric motor fitted with a worm-reducing gear and a chain drive from this to the stirrer-shaft drive, which ran in bearings on a brass strip attached to the outer bath and was joined to the main propeller shaft by means of a dog clutch. In this way it was possible to get a slow and very uniform rate of stirring.

The submarine was supported on a copper tripod with raised edges and clamped to the bottom of the bath. The submarine jacket rested on this, and was held in position by two rods from the cross-bar of the bath clamped down on top of the lid.

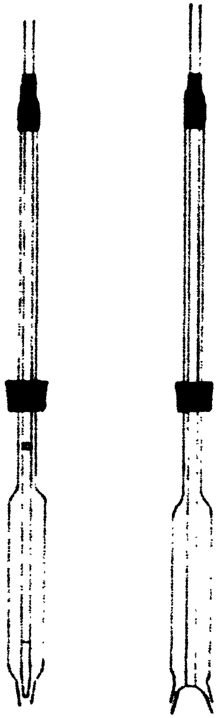
The outer bath was filled with light lubricating oil so that a wire-resistance heater could be used for raising the temperature of the bath quickly. This heater consisted of eleven yards of 22 S.W.G. nickel chrome wire wound over a frame made up from two "Syndano" strips of one-quarter of an inch thickness, spaced about 10 inches apart by means of half-inch brass bolts. The "Syndano" strips were made with V-nicks along one edge about one-quarter of an inch apart, and had holes drilled along their length along the middle to correspond with the V-nicks. The wire was then threaded through the nicks so that the heater then took the form of a double mat of parallel wires 10 inches long.

The bath also contained a 240-watt heating lamp and a toluene thermo-regulator, so that the temperature could be kept constant at any desired point within ±0·05° C. The oil was very vigorously stirred by means of a fast-running propeller stirrer driven by means of an electric motor.

The Introduction of Solid or Liquid into the Calorimeter.

Solid or liquid was introduced into the calorimeter when it was set up by means of glass pipettes with long stems

Fig. 3.



(fig. 3). The pipette for delivering liquid was similar to that described by Dürr and Lange (*Zeit. physik. Chem.* cxxi. p. 361, 1926). The pipette with a long stem was closed by a ground-glass rod sealed to a tube running inside the pipette stem and almost touching it. This tube had an opening communicating with the inside of the pipette. The long tube attached to the ground stopper and the stem of the pipette were joined at the top by means of an indiarubber sleeve. By placing the nozzle of the pipette in a liquid and drawing up the glass tube the pipette could be filled by sucking at the top of the glass tube. This glass tube was now pushed down and the pipette closed. A cap was placed over the top of the glass tube, and the liquid remaining on the outer walls was carefully wiped off, so that the pipette could now be weighed full of liquid. After fitting in the calorimeter through a rubber bung, the pipette could be opened and the liquid delivered quickly and without splashing. A similar method was used for the introduction of solid, except that the pipette was replaced by an arrangement similar to an inverted weighing bottle, the ground stopper of which could be pushed out by means of the arrangement described.

The Thermometers.

The two Beckmann thermometers used were carefully compared over the whole length of their scale with a thermometer reading to 0·01°, calibrated by the German Reichsanstalt. The thermometers were compared in positions corresponding to those in which they were to be used. They were read by means of a hand-lens to ±0·001°, but the probable accuracy is not more than ±0·005° on account of the sticking of the mercury. The thermometers were tapped by hand for some moments before a reading was taken.

Manipulation of the Apparatus.

A known weight of solvent was introduced into the calorimeter, and the weighed pipette containing a known weight of salt or solvent according to the experiment was then introduced. The apparatus was then left stirring for some hours until an equilibrium had been set up between the calorimeter and the outer bath, and the difference of temperature then prevailing was taken as that required to maintain the adiabatic condition for that experiment. As others have pointed out, the heating effect due to stirring is not constant over a series of experiments, and it varies among other things with the volume and concentration of the liquid stirred, and therefore the difference in temperature required to maintain the adiabatic condition between the inner and outer vessels necessarily alters over a series of readings.

A series of readings was now taken over some minutes of the temperatures of the inner and outer vessels, and at the proper moment the solid or liquid was allowed to enter the liquid in the calorimeter. The temperature now either rose or fell. In the case of rising temperature, the heater in the outer bath was quickly switched on in order to maintain the adiabatic condition. With the quicker temperature changes the adiabatic condition could not be kept so accurately during the initial stages, and so the rate of leakage for a given thermal head was afterwards found for the solution, and by this means a correction was applied.

In cases of falling temperature the apparatus was used isothermally. The heater was switched on at a noted time in order to keep the temperature constant as far as possible. At the same time the fall of potential across the heater and that across the standard ohm were quickly measured. In some cases it was not possible to supply the large quantity of heat required quickly enough to prevent the temperature of the contents from falling. In these cases the correction obtained as described from the rate of thermal leakage was applied. The largest correction applied in this way was about 4 per cent. of the total heat absorbed.

At this stage another series of measurements of temperature was taken over some minutes to see that the temperature has actually become constant. At the end of this time the pipette was quickly and carefully withdrawn and made ready for another observation.

The method of calculation will be illustrated by an experiment requiring a large correction for failure to hold the adiabatic condition and the overshooting of the isothermal.

In an experiment 8·9318 grams of potassium chloride were dissolved in a solution containing 66·5862 grams of potassium chloride in 391·42 grams of water.

The initial temperature as read on the Beckmann thermometer was 2·837° C., the final temperature was 2·871° C. The isothermal correction is thus +0·034° C. In addition the adiabatic condition was not accurately kept at the beginning of the experiment. The temperature of the calorimeter contents and the temperature were plotted against time on the same diagram. The deviations from the adiabatic conditions may now be summed in the form of a mean value for a constant thermal head for a given time, in this case 0·400° C. for seven minutes. The fundamental equation for temperature loss is

$$\eta = \phi KT,$$

where η is temperature loss, ϕ is the thermal head, T is the length of the experimental period, and K is a multiplier of the thermal head or the thermal leakage modulus. At the conclusion of the experiment proper the temperatures of the bath and calorimeter contents were arranged so that there was a thermal head of 0·124° C. between them. The rate of thermal leakage was found to be 0·000611° C. per minute.

$$0{\cdot}000611 = K \times 0{\cdot}124.$$
$$\therefore \qquad K = 0{\cdot}0049283.$$

Therefore a head of 0·400° C. for seven minutes will give a temperature loss of

$$\eta = 0{\cdot}0049283 \times 0{\cdot}400 \times 7$$
$$= 0{\cdot}014^{\circ}\ C.$$

The isothermal correction was 0·034° C. and the adiabatic correction was 0·014° C., *i. e.* total correction 0·048° C. The water equivalent of the calorimeter and its contents was 474·795 cals./deg., and the correction is thus

$$474{\cdot}795 \times 0{\cdot}048 = 22{\cdot}790 \text{ gram calories.}$$

The heat supplied to the calorimeter contents was 460·988, and therefore the corrected heat of reaction was

$$460{\cdot}988 - 22{\cdot}790 = -438{\cdot}198 \text{ gram calories.}$$

The intermediate heat of solution was thus

$$\frac{-438{\cdot}198 \times 74{\cdot}56}{8{\cdot}9318} \text{ gram cals./mol} = -3658 \text{ gram cals./mol.}$$

The Measurements of the Heats of Solution.

The salts used were "Analytical Reagents," recrystallized and tested qualitatively for likely impurities.

For the preparation of ethyl alcohol, 96 per cent. ethyl alcohol was poured on to a large quantity of freshly burnt lime and allowed to stand over it for some days with periodical shaking. It was then fractionated, the first and last runnings being rejected. It was then allowed to stand over freshly cleaned and turned metallic calcium and was refractionated, the first and last runnings being again rejected, and was found free from aldehyde and ammonia. It was stored in a vessel with a siphon attachment and a guard tube of phosphorus pentoxide.

The density of the alcohol was $^{25^{\circ}}_{5^{\circ}}D = 0{\cdot}7849$.

1. POTASSIUM CHLORIDE IN WATER.

The pure salt was dried at 120° C. The weight of water used was 391·42 grams. The experimental results are given in Table III. W.E. denotes water equivalent.

TABLE III.*

Weight of a single portion of KCl.	W. E. (corr.), cals./deg.	Isothermal correction, ° C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols KCl}}{100 \text{ mols } H_2O}$.	Integral heat of solution, cals./mol.	Mean molar concentration, $\frac{\text{mols/KCl}}{100 \text{ mols } H_2O}$.	Intermed. heat of solution, cals./mol.
8·9990	458·482	−0·022	−514·875	0·5555	−4266	0·2777	−4266
6·1740	455·287	−0·004	343·547	0·9345	4229	0·7450	4149
8·0160	455·502	−0·012	440·536	1·4315	4178	1·1830	4101
7·2502	459·670	−0·012	388·109	1·8791	4132	1·6553	3991
9·0768	468·751	−0·048	480·083	2·4394	4089	2·1592	3944
8·7958	470·222	−0·010	456·066	2·9824	4048	2·7109	3866
8·6616	459·922	−0·017	440·571	3·5171	4010	3·2497	3784
9·6128	462·302	−0·022	479·052	4·1100	3967	3·8135	3716
8·0318	474·795	−0·048	438·198	4·6619	3931	4·3859	3658
8·9984	447·927	−0·024	435·534	5·2170	3896	4·9394	3600
9·2673	451·848	−0·002	436·923	5·7890	3859	5·508	3516
9·8539	453·177	−0·029	459·580	6·3980	3824	6·093	3477
From heat of dilution				7·082	3768	7·210	3399
				7·338	3752	7·692	3362
				8·045	3715	8·363	3312
				8·681	3687		

---

* In all the tables the sign at the top of a column, or in the column, refers to all values below, until a new sign is introduced.

The details necessary for the calculation of the water equivalent and the heat of reaction are given in Tables IV. and V.

TABLE IV.

Details for Determination of Water Equivalent.

Expt.	Drop in voltage across (a) heater,	(b) standard,' 1 ohm.	Time, secs.	Temp. diff. (corr.).	Water equivalent, cals./deg.
1	6·8380	0·4330	200·8	0·310	458·482
2	6·8770	0·4373	223·7	0·353	455·287
3	6·9120	0·4389	247·0	0·393	455·502
4	6·7719	0·4305	198·0	0·300	459·670
5	6·9780	0·4428	201·3	0·317	468·751
6	6·9480	0·4413	218·9	0·341	470·222
7	6·8790	0·4372	207·4	0·324	459·922
8	6·8800	0·4367	195·8	0·304	462·302
9	6·9660	0·4425	257·9	0·400	474·795
10	6·9050	0·4390	320·4	0·518	447·927
11	6·8280	0·4344	281·85	0·442	451·848
12	6·8720	0·4385	254·95	0·405	453·177
13	6·8790	0·4359	204·95	0·334	439·571
14	6·7039	0·4040	215·35	0·323	431·386
15	5·5652	0·3555	272·4	0·398	407·251
16	6·8770	0·4373	191·35	0·310	446·640

TABLE V.

Details for Determination of Heat of Reaction.

Expt.	Voltage drop across (a) heater,	(b) standard, 1 ohm.	Time, secs.	Heat of reaction uncorrected, in cals.
1	6·6058	0·4207	760·3	−504·778
2	6·8880	0·4378	479·4	345·368
3	6·9370	0·4401	611·5	446·002
4	6·9020	0·4379	545·15	393·624
5	6·9830	0·4431	679·9	502·583
6	6·9530	0·4416	628·15	460·768
7	6·8820	0·4372	623·8	448·390
8	6·8670	0·4365	683·05	489·123
9	6·9320	0·4422	629·5	460·988
10	6·9120	0·4391	615·5	446·284
11	6·8360 6·8510	0·4345 0·4352	174·6 438·2	123·894 312·128
12	6·8710 6·8640 6·8570	0·4390 0·4388 0·4387	392·7 137·3 126·55	282·983 98·794 90·945
13	3·0798	0·1948	128·95	18·482
14	3·0798	0·1977	255·15	37·114
15	3·0728	0·1952	203·9	29·218
16	4·5546	0·2873	253·65	79·294

For the determination of the total heat of solution L_s, the heat of dilution of 36·33 grams of potassium chloride solution saturated at 25° C. (containing 9·6062 grams KCl in 26·72 grams of water) with 400 grams of water was measured.

Heat of dilution $= -74·471$ cals.

This forms a solution containing 9·6062 grams of potassium chloride in 426·72 grams of water. If we now imagine this solution to be prepared from salt and water, we can find the integral heat of this solution from the curve connecting the integral heats of solution already found. From these two values simple calculation gives the value for the total heat of solution $L_s = -3687$ cals. per mol of potassium chloride. By combining this value for the total heat of solution with the heats of dilution obtained in the region of saturation, we obtain three values for the integral heat of solution L_c and the differential heat of solution Λ_c, at these concentrations. 302·628 grams of a saturated solution of potassium chloride at 25° C. were diluted three times with a known weight of water. The results obtained are added to the heats of solution directly determined in Table III. The curves connecting the heats of solution with concentration have been drawn for potassium chloride with the values of Table III. The curve for the mean intermediate heat of solution is practically a straight line, and so may be used without correction for curvature to give the values of the differential heat of solution. Extrapolation to the saturation point gives a value for the *final heat of solution*, $\Lambda_s = -3291$ cals. per mol of potassium chloride. Further, the production of the curves for the integral heat of solution and the differential heat of solution give a value for the *first heat of solution*, $L_0 = -4315$ cals. per mol of potassium chloride. Also, by means of the formula $\phi_c = c(L_c - \Lambda_c)$, we may calculate from both curves the *differential heat of dilution* ϕ_c and also the *first heat of dilution*, $\phi_s = -34·41$ cals. per mol of water. The final values are collected in Table VI.

Comparison with previous Results.

The agreement of these values with those of Wust and Lange (*l. c.*) is quite satisfactory, since the accuracy of the present results is probably not so great as in their case. The results are compared in Table VII. There is also fairly good agreement with some results of Brönsted (*Zeit. für physik. Chem.* lvi. p. 663, 1906), although in this lower concentration range the agreement is not so good as in the

TABLE VI.

The Heats of Solution and Dilution of Potassium Chloride in Water at 25° C.

Concentration, $\frac{\text{mols KCl}}{\text{100 mols } H_2O}$.	Integral heat of solution, cals./mol KCl.	Differential heat of solution, cals./mol KCl.	Differential heat of dilution, cals./mol H_2O.
0·0	L_0 −4315	−4315	−0·00
0·5	4268	4214	0·30
1·0	4218	4100	1·22
1·5	4168	4020	2·295
2·0	4126	3942	3·680
2·5	4087	3877	5·250
3·0	4048	3811	7·110
3·5	4007	3744	9·205
4·0	3974	3672	12·06
4·5	3938	3628	13·95
5·0	3906	3585	16·05
5·5	3873	3540	18·315
6·0	3839	3495	20·64
6·5	3805	3448	23·205
7·0	3773	3415	25·08
7·5	3743	3377	27·45
8·0	3718	3338	30·40
8·5	3694	3302	33·32
8·691	3687	3291	34·41

$L_0 = -4315$; ; $L_s = -3687$; $\Lambda_s = -3291$: $\phi_s = -34{\cdot}41$.

TABLE VII.

Concentration, mols/KCl 100 mols H_2O.	L_c, cals. mol KCl, present values.	L_c, cals. mol KCl, Wust and Lange.
0·0	−4315	−4285
0·5	4268	4245
1·0	4218	4205
1·5	4168	4165
2·0	4126	4123
2·5	4087	4082
3·0	4048	4043
3·5	4007	4004
4·0	3974	3966
4·5	3938	3930
5·0	3906	3894
5·5	3873	3860
6·0	3839	3828
6·5	3805	3798
7·0	3773	3770
7·5	3743	3743
8·0	3718	3720
8·5	3694	3700
8·691	3687	3692

higher concentrations. Brönsted's measurements were made at a temperature of 25·04° C. In Table VIII. the results are compared with those of Brönsted and with those of Wust and Lange for the same concentrations.

TABLE VIII.

Concentration, $\frac{\text{mols KCl}}{\text{100 mols H}_2\text{O}}$.	L_c, cals./mol KCl, present values.	L_c, cals./mol KCl, Brönsted.	L_c, cals./mol KCl, Wust and Lange.
0·167	−4302	−4266	−4273
0·333	4285	4255	4258
0·499	4268	4246	4245
0·667	4257	4235	4233
0·833	4235	4224	4218

These results probably show the limits of accuracy of the apparatus, since they were the first obtained, without any practice in manipulation. Among others, values have been obtained by Holluta and Werner (*Zeit. für physik. Chem.* cxxix. p. 262, 1927), who for a concentration of 1·107 mols KCl per 100 mols of water give 4216·1 cals., while the present curve gives 4210 cals.

Berthelot and Ilosvay (*Ann. de chim. et de phys.* xxix. p. 295, 1883), at a temperature of 18·5° C. and concentration 1 mol KCl per 100 mols water, give −4305 cals. By means of a formula for the temperature coefficient the value at 25° C. would be found to be −4136 cals. per mol of potassium chloride, while the present value is −4218. The difference is quite within the limits of accuracy attainable by these authors.

2. POTASSIUM THIOCYANATE IN WATER.

The pure salt was dried at 140° C. in an electric oven. The weight of water used was 349·36 grams. The results are given in Table IX.

The water equivalent and heat of reaction were calculated as before, and in this and all subsequent cases details will be found in the thesis of W. E. Soper, in the University of London, 1928.

The total heat of solution L_s was determined as before from dilution experiments. 34·18 grams of a saturated solution (at 25° C.) of potassium thiocyanate in water (containing 23·91 grams of potassium thiocyanate per

TABLE IX.

Weight of a single portion of KONS.	W. E. (corr.), cals./deg.	Isothermal correction, °C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols KCNS}}{\text{100 mols } H_2O}$.	Integral heat of solution, cals./mol.	Mean molar concentration, $\frac{\text{mols KONS}}{\text{100 mols } H_2O}$.	Intermed. heat of solution, cals./mol.
8·5289	399·308	−0·031	−509·664	0·489	−5807	0·244	−5807
5·3256	391·925	−0·019	306·473	0·794	5724	0·642	5592
5·3254	394·875	−0·018	302·796	1·100	5669	0·947	5525
4·3218	397·321	−0·016	231·916	1·347	5585	1·223	5214
4·9438	398·577	−0·013	273·241	1·627	5561	1·487	5371
7·5628	387·271	−0·065	416·511	1·781	5557	1·558	5352
7·2498	386·130	−0·011	388·262	2·210	5178	1·995	5204
9·0490	381·488	−0·004	464·090	2·746	5382	2·478	4984
7·6404	395·051	−0·005	383·851	3·199	5311	2·972	4882
8·1138	379·051	−0·002	393·716	3·680	5233	3·439	4715
8·0698	381·525	−0·002	383·802	4·157	5163	3·918	4622
7·9192	384·206	−0·004	371·026	4·626	5101	4·392	4553
9·1110	384·761	−0·001	414·887	5·166	5031	4·896	4425
8·1463	386·034	−0·006	362·457	5·648	4970	5·407	4324
				28·18	3521		
						29·26	2818
				30·35	3463		
						31·99	2718
				33·63	3406		
From dilution experiments						34·72	2713
				35·80	3355		
						37·50	2665
				39·21	3295		
						41·25	2647
				43·29	3235		

10·27 grams of water) was added to 370·1 grams of water, and the heat of dilution measured.

Heat of dilution	−597·890 cals.
Heat of solution from L_c curve.	−1393·875 cals.
Total heat of solution (calcd.).	−3235 cals./mol. KCNS.

Five intermediate heats of dilution have been combined with this value of the total heat of solution. They were obtained by diluting with five separate weighed quantities of water (about 12 grams) 407·210 grams of a saturated solution (containing 284·920 grams KCNS in 122·29 grams of water).

TABLE X.

Expt.	1.	2.	3.	4.	5.
Weight of water added, grms....	12·4317	12·8408	13·1762	13·3330	13·3556
Heat of dilution, cals.	−175·358	−175·991	−167·890	−167·885	−166·066

From these results and from the value of the total heat of solution L_s, values for the integral heats of solution L_c, and for the differential heats of solution Λ_e, may be calculated. The values are given in the table of experimental results (Table IX.).

The experimental values were plotted against concentration, and the differential heat of solution obtained from the curves, together with the extrapolated values for the first heat of solution. The first heat of dilution and the differential heat of dilution were obtained as before. The final values are given in Table XI.

No previous measurements have been found at this temperature, and, indeed, the only previous measurement is that given in Landolt-Börnstein's *Tabellen*, due to Joannis at 13° C., and concentration of 1 mol of potassium thiocyanate to 200 mols water, who gives −6·1 kilog. calories.

Discussion of the Results for Potassium Thiocyanate and Water.

The curves for potassium thiocyanate and water are quite regular and free from any characteristics. The heat of solution is negative.

It was not possible to obtain any values for potassium thiocyanate and ethyl alcohol, since the solubility is not very great and the process of solution is very slow. It was, however, found that the heat of solution of potassium thiocyanate in ethyl alcohol is negative in sign as far as it could be observed.

TABLE XI.

Heats of Solution and Dilution of Potassium Thiocyanate in Water at 25° C.

Concentration, $\frac{\text{mols KCNS}}{\text{100 mols H}_2\text{O}}$*	Integral heat of solution L_c, cals./mol KCNS.	Differential heat of solution A_c, cals./mol KCNS.	Differential heat of dilution ϕ_c, cals./mol H_2O.
0·0	−5988	−5988	0·0
0·5	5795	5693	−0·51
1·0	5693	5494	1·99
1·5	5603	5325	4·17
2·0	5508	5157	7·02
2·5	5422	5003	10·475
3·0	5339	4859	14·40
3·5	5258	4727	15·585
4·0	5185	4614	22·84
4·5	5115	4492	28·035
5·0	5050	4380	33·50
5·5	4985	4270	39·325
……	……	……	……
30·0	−3470	−2792	−203·4
31·0	3447	2762	212·35
32·0	3426	2736	220·8
33·0	3406	2716	227·7
34·0	3387	2699	233·9
35·0	3368	2685	233·9
36·0	3350	2674	239·05
37·0	3332	2667	246·05
38·0	3314	2661	248·14
39·0	3298	2656	250·38
40·0	3281	2651	252·00
41·0	3267	2647	254·20
42·0	3252	2644	255·36
43·0	3239	2641	257·14
43·291	3235	2640	257·58

$L_0 = -5988$; $L_s = -3235$.

3. SODIUM THIOCYANATE IN WATER.

The pure salt was recrystallized and dried by heating to 140° C. The weight of water used was 348·00 grams. The results are given in Table XII.

TABLE XII.

Weight of a single portion of NaCNS.	W. E (corr.), cals./deg.	Isothermal correction, ° C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols NaCNS}}{\text{100 mols H}_2\text{O}}$.	Integral heat of solution, cals./mol.	Mean molar concentration, $\frac{\text{mols NaCNS}}{\text{100 mols H}_2\text{O}}$.	Intermed. heat solution, cals./mol.
4·7950	401·423	−0·017	−99·232	0·306	−1678	0·153	−1678
5·2886	405·782	−0·005	102·568	0·644	1622	0·475	1573
5·9389	403·858	−0·000	100·270	1·023	1574	0·833	1495
6·7007	407·977	−0·026	113·138	1·451	1514	1·237	1369
6·1119	399·600	−0·013	91·415	1·841	1450	1·646	1213
5·7219	401·737	−0·001	79·259	2·207	1396	2·024	1123
From dilution experiments				19·37	−428		
						20·12	603
				20·98	445		
						21·87	609
				22·77	463		
						23·88	681
				25·00	486		
						26·55	873
				28·11	521		

The total heat of solution was determined, as before, from dilution experiments. 26·5556 grams of a saturated solution of sodium thiocyanate at 25° C. (containing 14·6649 grams of sodium thiocyanate in 11·8907 grams of water) was diluted with 329·65 grams of water.

Heat of dilution	−191·727 cals.
Heat of solution from L_c curve.	−285·979 cals.
Total heat of solution (calcd.) .	−521 cals./mol NaCNS

Four intermediate heats of dilution have been combined with this value of the total heat of solution. They were obtained by diluting with four separate weighed quantities of water (about 12 grams) 308·480 grams of a saturated solution of sodium thiocyanate at 25° C. (containing 164·605 grams of sodium thiocyanate in 133·805 grams of water).

TABLE XIII.

Expt.	1.	2.	3.	4.
Weight of water added, grams.	12·8760	14·3432	13·6866	14·7423
Heat of dilution, cals.	−97·225	−49·200	−35·663	−34·543

From these results and from the value of the total heat of solution the values of the integral heats of solution at these concentrations may be calculated. The values are added to Table XII.

The experimental values have been plotted against concentration, and the first heat of solution and values for the differential heats of solution obtained. The final values are added to Table XIV.

TABLE XIV.

Heats of Solution and Dilution of Sodium Thiocyanate in Water at 25° C.

Concentration, $\frac{\text{mols NaCNS}}{\text{100 mols H}_2\text{O}}$	Integral heat of solution L_c, cals./mol NaCNS.	Differential heat of solution, cals./mol NaCNS.	Differential heat of dilution, cals./mol H_2O.
0·0	−1677	−1677	0·0
0·5	1648	1571	−0·38
1·0	1574	1426	1·45
1·5	1500	1268	3·48
2·0	1425	1118	6·24

……

TABLE XIV. (*continued*).

Heats of Solution and Dilution of Sodium Thiocyanate in Water at 25° C.

Concentration, $\frac{\text{mols NaCNS}}{\text{100 mols } H_2O}$	Integral heat of solution L_c, cals./mol NaCNS.	Differential Heat of solution, cals./mol NaCNS.	Differential heat of dilution, cals./mol H_2O.
20·0	434	These values are indefinite, since the curve goes through a maximum and there are not enough points to decide the course of the curve.	
20·5	439		
21·0	444		
21·5	450		
22·0	455	−612	+36·30
22·5	460	625	37·12
23·0	465	640	40·25
23·5	470	651	42·50
24·0	476	687	50·64
24·5	481	716	57·57
25·0	486	751	66·25
25·5	493	788	75·225
26·0	500	827	85·02
26·5	507	868	95·665
27·0	514	909	106·65
27·47	521	947	117·02

$L_0 = -1677$: $L_s = -521$; $\Lambda_s = -947$; $\rho_s = +117·02$.

There are no previous measurements to compare with the present values.

4. THE HEAT OF SOLUTION OF SODIUM THIOCYANATE IN ETHYL ALCOHOL.

The pure salt was carefully dried at 140° C. in an electric oven after being recrystallized several times from water. The weight of ethyl alcohol used was 258·08 grams. The experimental results are given in Table XV.

The total heat of solution was obtained, as before, from dilution experiments. A saturated solution of sodium thiocyanate in ethyl alcohol at 25° C. (containing 2·6832 grams of sodium thiocyanate in 12·7292 grams of ethyl alcohol) was diluted with 270·20 grams of ethyl alcohol.

Heat of dilution	70·122 cals.
Heat of solution from L_c curve.	36·803 cals.
Total heat of solution (calcd.)	−1007 cals./mol NaCNS

TABLE XV.

Heats of Solution of Sodium Thiocyanate in Ethyl Alcohol at 25° C.

Weight of a single portion of NaCNS.	W. E. (corr.), cals./deg.	Isothermal correction or temp. rise.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols NaCNS}}{100 \text{ mols EtOH}}$.	Integral heat solution, cals./mol.	Mean molar concentration, $\frac{\text{mols NaCNS}}{100 \text{ mols EtOH}}$.	Intermed. heat solution, cals./mol.
6·0357	226·500	0·335	+75·877	1·203	+1019	0·601	+1019
4·3938	226·155	0·159	35·959	2·074	871	1·638	648
4·0689	230·744	0·080	18·460	2·889	729	2·481	368
5·9800	238·124	0·050	11·906	4·081	563	3·985	161
5·9988	239·029	−0·032	−25·684	5·276	357	4·678	−330
5·3684	241·470	−0·005	−44·636	6·346	183	5·811	−674
5·8350	240·591	0·004	−68·833	7·509	6·5	6·927	−956
From dilution experiments				8·814	−769		
						8·897	−1417
				9·164	−793		
						9·334	−1474
				9·505	−818		
						9·721	−1540
				9·938	−849		
						10·114	−1620
				10·391	−884		
						10·643	−1705
				10·896	−922		
						11·106	−1788
				11·416	−961		
						11·693	−1934
				11·970	L_s −1007		

The last three values in column 3 are isothermal corrections.

Seven successive intermediate heats of dilution were measured, starting from the saturated solution, and combined with this value for the total heat of solution. 253·64 grams of a saturated solution of sodium thiocyanate in ethyl alcohol at 25° C. (containing 44·156 grams of sodium thiocyanate in 209·484 grams of ethyl alcohol) were diluted successively with seven weighed quantities of ethyl alcohol.

From these results, and from the value of the total heat of solution, the values for the integral heats of solution may be calculated for these concentrations, as well as the mean intermediate heats of solution. The values obtained are added to the experimental results in Table XV.

Table XVI.

Expt.	Weight of alcohol added, grams.	Heat of dilution, cals.
1	10·2545	+24·792
2	10·4948	21·553
3	11·1688	20·741
4	11·0273	18·595
5	11·4903	17·149
6	9·8038	13·314
7	10·8691	13·563

The experimental values have been plotted against concentration, and the final values in Table XVII. have been

Table XVII.

Heats of Solution and Dilution of Sodium Thiocyanate in Ethyl Alcohol at 25° C.

Concentration, mols NaCNS 100 mols EtOH	Integral heat of solution L_c, cals./mol NaCNS.	Differential heat of solution A_c. cals./mol NaCNS.	Differential heat of dilution ϕ_c, cals./mol EtOH.
0·0	+1195	+1195	0·0
0·5	1117	1050	+0·33
1·0	1035	860	1·75
1·5	955	693	3·93
2·0	875	550	7·50
2·5	795	364	8·83
.....	.....	.....	.....
9·0	−790	−1427	+57·33
9·5	815	1514	66·40
10·0	848	1615	76·70
10·5	885	1705	86·10
11·0	920	1800	96·80
11·5	964	1896	107·18
11·970	1007	1992	117·90

$L_0=+1195$; $L_s=-1007$; $A_s=-1992$; $\phi_s=+117·90$.

obtained from these curves. By extrapolation we also obtain the final heat of solution, the first heat of solution, and the differential heat of solution.

Discussion of Results with Sodium Thiocyanate.

The curve drawn for the differential heat of solution of sodium thiocyanate in water passes through a maximum value. Similar curves were found for the chloride, bromide, and iodide of sodium by Wust and Lange.

An examination of the curves for sodium thiocyanate and ethyl alcohol shows that at lower concentrations the heat of solution is positive in sign, but with rising concentration the value becomes smaller, and finally becomes negative in sign. This might possibly point to the existence of an alcoholate at lower concentrations, but as yet it has not been isolated.

5. THE HEAT OF SOLUTION OF ANHYDROUS CUPRIC CHLORIDE IN WATER.

The pure salt was recrystallized from water, and dehydrated and dried by heating in an electric oven at 140° C. The weight of water used was 340·35 grams. The experimental results are given in Table XVIII.

The total heat of solution was obtained, as before, from dilution experiments. A saturated solution of cupric chloride in water (containing 10·7751 grams of $CuCl_2$ in 14·3643 grams of water) was diluted with 387·67 grams of water.

Heat of dilution	405·994 cals.
Heat of solution from L_e curve.	894·849 cals.
Total heat of solution (calcd.)...	6247 cals./mol $CuCl_2$

Four successive intermediate heats of dilution of the saturated solution have been made and combined with this value for the total heat of solution. 542·26 grams of a saturated solution of cupric chloride in water at 25° C. (containing 233·496 grams of cupric chloride ($CuCl_2$) in 308·764 grams of water) were diluted successively with four weighed quantities of water.

TABLE XVIII.

Heat of Solution of Anhydrous Cupric Chloride in Water at 25° C.

Weight of a single portion of $CuCl_2$.	W. E. (corr.). cals./deg.	Temperature rise, ° C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols } CuCl_2}{100 \text{ mols } H_2O}$.	Integral heat solution, cals./mol.	Mean molar concentration, $\frac{\text{mols } CuCl_2}{100 \text{ mols } H_2O}$.	Intermed. heat solution, cals./mol.
3·0566	409·495	0·643	+263·305	0·120	+11724	0·060	+11724
3·8322	412·313	0·781	322·017	0·271	11590	0·195	11387
4·6039	417·830	0·908	379·390	0·452	11355	0·361	11082
3·6724	397·686	0·707	281·164	0·593	11193	0·522	10671
3·9836	406·092	0·760	308·630	0·750	11031	0·672	10120
3·9720	391·353	0·750	293·515	0·906	10865	0·828	10071
3·5679	396·564	0·650	257·767	1·046	10711	0·976	9716
				8·713	6607		
						8·809	4218
				9·027	6515		
						9·185	4092
From dilution experiments......				9·344	6438		
						9·513	4033
				9·683	6349		
						9·866	3873
				10·049	6247		

TABLE XIX.

Expt.	Weight of water added, grams.	Heat of dilution.
1	13·5225	+177·370
2	12·4666	155·170
3	10·9380	133·064
4	13·3365	169·987

From these values and from the value of the total heat of solution the values for the integral heats of solution at these concentrations was obtained. The values obtained are added to the experimental values in Table XVIII. The experimental values have been plotted against concentration, and the final values were taken from these. The final values are given in Table XX. By extrapolation we obtain the final heat of solution, the first heat of solution, and the differential heats of dilution at saturation.

TABLE XX.

The Heats of Solution and Dilution of Anhydrous Cupric Chloride at 25° C.

Concentration. $\frac{\text{mols } CuCl_2}{\text{100 mols } H_2O}$.	Integral heat of solution L_c, cals./mol $CuCl_2$.	Differential heat of solution A_c, cals./mol $CuCl_2$.	Differential heat of dilution ϕ_c, cals./mol H_2O.
0·0	+11850	+11850	0·0
0·5	11300	10754	+2·73
1·0	10763	9658	11·65
....	....	....	....
8·5	+6663	+4162	+212·58
9·0	6528	4110	217·58
9·5	8394	4020	225·53
10·0	6259	3802	245·70
10·049	6247	3778	248·11

$L_0 = +11850$; $L_s = +6247$; $A_s = +3778$; $\phi_s = +248·11$.

Comparison with previous Values.

The only previous value is due to Thomsen at concentration 0·167 mol $CuCl_2$ per 100 mols of water, and is 11080 cals./mol., the value in the present work being 11625.

6. HEAT OF SOLUTION OF ANHYDROUS CUPRIC CHLORIDE IN ETHYL ALCOHOL.

The pure salt was recrystallized, dehydrated, and dried as before. It was carefully and quickly put into a dried and weighed pipette and weighed again. The weight of ethyl alcohol used was 251·870 grams. The experimental values are given in Table XXI.

TABLE XXI.

Weight of a single portion of $CuCl_2$.	W. E. (corr.). cals./deg.	Temperature rise, ° C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols } CuCl_2}{100 \text{ mols } EtOH}$.	Integral heat solution, cals./mol.	Mean molar concentration, $\frac{\text{mols } CuCl_2}{100 \text{ mols } EtOH}$.	Intermed. heat solution, cals./mol.
5·8759	215·220	1·001	+215·436	0·799	+4931	0·400	+4931
4·6276	215·745	0·736	158·786	1·428	4792	1·113	4615
4·5658	213·305	0·705	150·380	2·049	4693	1·738	4430
5·0588	211·073	0·761	160·621	2·737	4578	2·393	4270
4·0896	211·959	0·593	125·692	3·293	4514	3·015	4133
4·3124	216·569	0·603	130·591	3·879	4438	3·586	4073
4·5458	217·671	0·613	133·432	4·497	4371	4·188	3948
From dilution experiments				11·91	3626		
						12·16	2915
				12·42	3597		
						12·68	2884
				12·95	3560		
						13·27	2634
				13·60	3516		
						13·90	2503
				14·20	3473		
						14·56	2430
				14·93	3422		
						15·32	2248
				15·71	3364		
						16·12	2188
				16·52	3307		
						17·02	2180
				17·52	3243		

The total heat of solution was obtained, as before, from dilution experiments. A saturated solution of anhydrous cupric chloride in ethyl alcohol at 25° C. (containing 4·8554 grams of $CuCl_2$ in 10·0146 grams of ethyl alcohol) was diluted by 258·73 grams of ethyl alcohol.

Heat of dilution	62·211 cals.
Heat of solution from L_c curve.	179·284 cals.
Total heat of solution (calcd.)...	3243 cals./mol $CuCl_2$

Eight successive intermediate heats of dilution of the saturated solution were made and combined with this value for the total heat of solution. 285·73 grams of a saturated solution of anhydrous cupric chloride in ethyl alcohol at 25° C. (containing 96·69 grams of $CuCl_2$ in 189·04 grams of ethyl alcohol) were diluted successively with eight weighed quantities of alcohol.

TABLE XXII.

Expt.	Weight of ethyl alcohol added, grams.	Heat of dilution. cals.
1	11·4598	+46·236
2	10·2208	40·994
3	11·0205	41·910
4	11·5225	37·087
5	10·1432	30·367
6	12·3432	32·172
7	10·7746	25·933
8	11·4326	21·114

From these results and from the total heat of solution the values for the integral and mean intermediate heats of solution are calculated for these concentrations. The values obtained are added to the values determined experimentally in Table XXI. The experimental values have been plotted against concentration, and the final values in Table XXIII. obtained. The first heat of solution and the final heat of solution are obtained by extrapolation, and the differential heat of dilution by the simple calculation used previously.

TABLE XXIII.

Heats of Solution and Dilution of Anhydrous Cupric Chloride in Ethyl Alcohol at 25° C.

Concentration, mols $CuCl_2$ 100 mols EtOH	Integral heat of solution L_c, cals./mol $CuCl_2$	Differential heat of solution, cals./mol $CuCl_2$.	Differential heat of dilution, cals./mol H_2O.
0·0	+5126	+5126	+0·0
0·5	4996	4875	0·6
1·0	4882	4665	2·17
1·5	4780	4490	4·35
2·0	4685	4360	6·50
2·5	4618	4245	9·32
3·0	4548	4134	12·42
3·5	4483	4075	14·28
………	………	………	………
14·0	3489	2975	71·96
15·0	3416	2551	129·75
16·0	3343	2296	167·52
17·0	3277	2182	186·12
17·5	3244	2175	186·87
17·52	3243	2176	186·94

$L_0 = +5126$: $L_s = +3243$; $\lambda_s = +2176$; $\varphi_s = +186·94$.

Discussion of the Results with Cupric Chloride.

In the case of water the first heat of solution is very high and positive in sign. With rising concentration the value for the heat of solution diminishes fairly rapidly, but it always remains comparatively high. With ethyl alcohol the heat of solution is positive in sign, but it does not vary so rapidly with rising concentration, although it does fall. Cupric chloride forms a stable hydrate, $CuCl_2 . 2H_2O$ with water, and a stable alcoholate with ethyl alcohol, $CuCl_2 . 2EtOH$ (see Lloyd, Brown, Bonnell, and Jones, J. Chem. Soc. p. 658, 1928). This would probably account for the high positive values for the heat of solution.

7. THE HEAT OF SOLUTION OF ANHYDROUS CALCIUM NITRATE IN WATER.

The pure salt was recrystallized several times from water, dehydrated by gentle heating in an electric oven, and finally heated for some hours in the electric oven at a temperature exceeding 180° C. The weight of water used was 355·47 grams. The experimental results are given in Table XXIV.

TABLE XXIV.

Weight of a single portion of $Ca(NO_3)_2$.	W. E. (corr.), cals./deg.	Temperature rise, ° C.	Heat of reaction, cals.	Molar concentration, mols $Ca(NO_3)_2$ / 100 mols H_2O	Integral heat solution, cals./mol.	Molar concentration, mols $Ca(NO_3)_2$ / 100 mols H_2O	Intermed. heat solution, cals./mol.
4·5948	388·337	·295	+114·559	0·142	+4129	0·071	+4129
4·1584	402·667	·269	108·318	0·271	4193	0·206	4264
7·0424	408·998	·460	188·138	0·489	4274	0·380	4373
6·1462	409·104	·412	168·551	0·679	4334	0·584	4489
6·8117	397·659	·480	190·878	0·890	4394	0·784	4587
6·2484	405·530	·452	183·300	1·084	4467	0·987	4802
From dilution experiments				11·715	5480	12·006	4549
				12·297	5436	12·596	4418
				12·896	5389	13·270	4230
				13·645	5326	14·084	4068
				14·523	5258		

The total heat of solution was determined, as before, from dilution experiments. A saturated solution of calcium nitrate in water at 25° C. (containing 16·1091 grams of $Ca(NO_3)_2$ in 12·2349 grams of water) was diluted by 336·65 grams of water.

Heat of dilution	−96·263 cals.
Heat of solution from L_c curve.	4280 cals./mol $Ca(NO_3)_2$
Total heat of solution (calcd.)	5258 cals./mol $Ca(NO_3)_2$

Four successive heats of dilution were measured and were combined with this value for the total heat of solution. 524·88 grams of a saturated solution of calcium nitrate in water at 25° C. (containing 297·625 grams of $Ca(NO_3)_2$ in 227·255 grams of water) were diluted successively with four weighed quantities of water.

TABLE XXV.

Expt.	1.	2.	3.	4.
Weight of water added in grams.	13·2236	13·5082	12·3702	13·2200
Heat of dilution in cals.	+126·524	+111·196	+85·944	+80·064

From these results and from the total heat of solution the values for the integral and mean intermediate heats of solution for these concentrations are easily calculated as before. The values are added to the experimentally determined values in Table XXIV. The experimental values have been plotted against concentration and the final values in Table XXVI. obtained from these curves. The first heat of solution and the final heat of solution are found by extrapolation, and the differential heat of dilution by calculation as before.

TABLE XXVI.

Heats of Solution and Dilution of Anhydrous Calcium Nitrate in Water at 25° C.

Concentration, mols $Ca(NO_3)_2$ 100 mols H_2O.	Integral heat of solution L_c, cals./mol salt.	Differential heat of solution A_c, cals./mol salt.	Differential heat of dilution ϕ_c, cals./mol H_2O.
0·0	+4074	+4074	0·0
0·5	4277	4443	−0·78
1·0	4437	4666	2·29
.....	.....	.....	.....
11·5	5495	4590	+104·07
12·0	5458	4516	113·04
12·5	5420	4424	124·5

TABLE XXVI. (*continued*).

Heats of Solution and Dilution of Anhydrous Calcium Nitrate in Water at 25° C.

Concentration, $\frac{\text{mols } Ca(NO_3)_2}{100 \text{ mols } H_2O}$.	Integral heat of solution L_c, cals./mol salt.	Differential heat of solution A_c, cals./mol salt.	Differential heat of dilution ϕ_c cals./mol H_2O.
13·0	5380	4306	138·32
13·5	5339	4189	155·25
14·0	5299	4070	172·08
14·5	5260	3954	189·37
14·523	5258	3948	190·35

$L_0 = +4074$; $L_s = +5258$; $A_s = 3948$; $\phi_s = +190·35$.

Comparison with previous Values.

Thomsen gives a value for 0·25 mol $Ca(NO_3)_2$ in 100 mols of water which is 3950 cals. per mol of salt. The value for this in the present work is 4184.

Pickering gives the two values for water:—

TABLE XXVII.

Concentration, $\frac{\text{mols } Ca(NO_3)_2}{100 \text{ mols } H_2O}$	L_c (Pickering).	L_c (present work).
0·404	+3940	+4246
0·408	3945	4248

8. THE HEATS OF SOLUTION OF ANHYDROUS CALCIUM NITRATE IN ETHYL ALCOHOL AT 25° C.

The purified salt was recrystallized several times from water, dehydrated by general heating, and finally heated to a temperature exceeding 180° C. for some hours. The weight of ethyl alcohol used was 313·85 grams. The experimental results are given in Table XXVIII.

The total heat of solution was determined as before. The saturated solution of anhydrous calcium nitrate in ethyl alcohol at 25° C. (containing 6·2576 grams of $Ca(NO_3)_2$ in 13·1273 grams of ethyl alcohol) was diluted by 313·52 grams of ethyl alcohol.

Heat of dilution	76·296 cals.
Heat of solution from L_c curve.	282·934 cals./mol salt
Total heat of solution (calcd.).	5406 cals./mol $Ca(NO_3)_2$

TABLE XXVIII.

Weight of a single portion, $Ca(NO_3)_2$.	W. E. (corr.) cals./deg.	Temperature rise, ° C.	Heat of reaction, cals.	Molar concentration, $\frac{\text{mols } Ca(NO_3)_2}{100 \text{ mols EtOH}}$.	Integral heat solution, cals./mol.	Mean molar concentration, $\frac{\text{mols } Ca(NO_3)_2}{100 \text{ mols EtOH}}$.	Intermed. heat solution, cals./mol.
1·6617	—	—	—	0·152	—	—	—
4·5024	239·705	0·847	+203·030	0·552	+7402	0·352	+7382
5·2171	239·213	0·946	226·295	1·020	7264	0·786	7101
4·6550	235·347	0·843	198·397	1·434	7197	1·227	6977
4·1882	240·958	0·725	174·694	1·813	7108	1·624	6828
5·0582	243·425	0·864	210·319	2·266	7048	2·039	6807
3·6726	243·815	0·615	149·946	2·596	7001	2·432	6684
2·8787	247·637	0·473	117·287	2·854	6955	2·675	6670
				11·157	5600		
						11·407	4763
				11·658	5564		
						11·913	4514
	From dilution experiments			12·168	5520		
						12·462	4369
				12·757	5467		
						13·084	4219
				13·411	5406		

Four successive heats of dilution of the saturated solution were made and combined with this value for the total heat of solution. 330·720 grams of a saturated solution of anhydrous calcium nitrate in ethyl alcohol at 25° C. (containing 106·759 grams $Ca(NO_3)_2$ in 223·961 grams of ethyl alcohol) were diluted by four weighed quantities of ethyl alcohol.

TABLE XXIX.

Expt.	1.	2.	3.	4.
Weight of water added in grams.	11·5429	11·3275	10·8146	11·5742
Heat of dilution in calories......	39·909	34·381	28·738	23·623

From these results and the value of the total heat of solution the values for the integral heat of solution and the mean intermediate heat of solution may be obtained for these concentrations. The values obtained are added to Table XXVIII. The experimental values have been plotted against concentration, and the final values in Table XXX. obtained in the curves. The first and final heats of solution were obtained by extrapolation from these curves, and the differential heat of dilution by means of the simple calculation used before.

TABLE XXX.

The Heats of Solution and Dilution of Anhydrous Calcium Nitrate in Ethyl Alcohol at 25° C.

Concentration, $\frac{\text{mols } Ca(NO_3)_2}{100 \text{ mols EtOH}}$.	Integral heat of Solution L_c. cals./mol salt.	Differential heat of solution A_c. cals./mol salt.	Differential heat of dilution ϕ_c. cals./mol EtOH.
0·0	+7584	+7584	0·0
0·5	7412	7244	+0·84
1·0	7280	7043	2·37
1·5	7170	6908	3·93
2·0	7084	6794	5·80
2·5	7018	6690	8·20
3·0	6935	6584	10·53
....	....	....	....
11·5	5579	4716	99·24
12·0	5533	4494	124·68
12·5	5489	4351	142·25
13·0	5443	4240	156·39
14·411	5406	4145	169·11

$L_0 = +7584$; $L_s = +5406$; $A_s = +4145$; $\phi_s = +169·11$.

Comparison with previous values.

Pickering obtained the following values :—

TABLE XXXI.

Concentration, mols $Ca(NO_3)_2$ 100 mols EtOH.	L_c (Pickering).	L_c (present work).
0·132	+7548	+7539
0·105	8708	7549
0·101	8711	7550

Discussion of the Results with Anhydrous Calcium Nitrate.

The heat of solution of anhydrous calcium nitrate in water is positive in sign. It rises with rising concentration to a maximum and then slowly falls. In the case of ethyl alcohol the value is positive, but greater than with water, and falls gradually with increasing concentration.

In this case, again, stable hydrates are known to exist. Graham (Phil. Mag. iv. pp. 265, 331, 1928) claimed to have isolated a crystalline alcoholate $2Ca(NO_3)_2$, 5EtOH. Lloyd, Brown, Bonnell, and Jones find $Ca(NO_3)_2 . 2EtOH$.

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XXVII. *Liquid Drops on the same Liquid Surface.* *By* J. B. SETH, *M.A.* (*Cantab.*), CHETAN ANAND, *M.A.* (*Punjab*), *and* LACHMAN DAS MAHAJAN, *M.Sc.* (*Punjab*) [*].

THE phenomenon of liquid drops formed and floating on the surface of the same liquid is of quite common occurrence. Thus, whenever a fine spray of water is falling on a surface of water, tiny drops of water can often be seen moving about on the water surface and finally coalescing with the general body of the liquid. The same effect is observed when a glass vessel containing some methylated spirit is bowed across its edge. A large number of drops, forming a regular pattern, are produced and remain floating on the surface for a short time, when they disappear in the body of the liquid. (A very familiar experiment described in text-books.) In the purification of aniline by distillation one often finds that a condensed drop, falling from the delivery tube, remains floating on the aniline surface in the receiving vessel for one or two seconds and then suddenly mixes with the liquid. Last year Professor Kataline published a paper * in which he gave an account of a demonstration of this phenomenon. He used a solution of fluorescin in water containing some gelatine, and obtained drops with a diameter up to about 6 mm. and having velocities from 10 to 30 cm. per second, which kept swimming on the surface for a period up to 6 seconds. He conclusively demonstrated that these were drops of the liquid and not mere bubbles.

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[*] Communicated by the Authors.

The object of the present investigation was to study in detail the conditions which make the formation of the floating drops easy, their size larger, and their lives longer. A large number of liquids have been tried and their properties studied, and a brief summary of the work is given below. By using suitable liquids under favourable conditions it has been possible to obtain floating drops as large as 12 mm. in diameter, and drops which kept floating on their liquid surface for nearly five minutes.

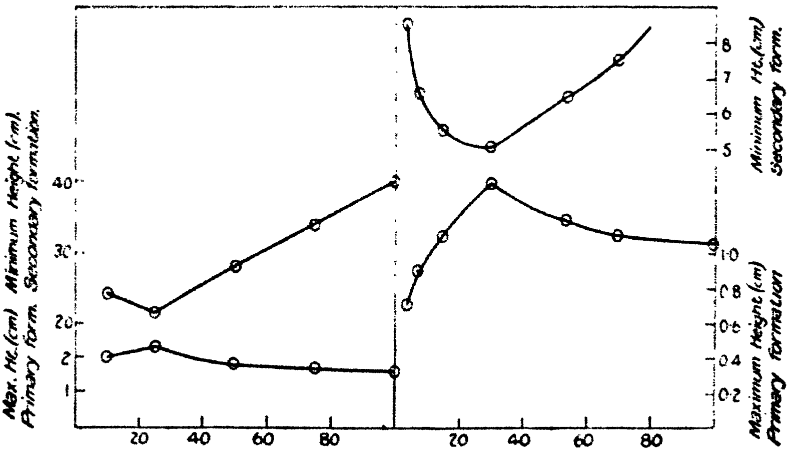
The easiest and most commonly applicable method of producing the drops is to fill the liquid in a burette and to allow it to flow down, drop by drop, on the surface of the same liquid kept in a suitable basin. The drops that float on the surface of the liquid can be classified under two headings: primary drops and secondary drops. The primary drops are obtained when the liquid is allowed to come down drop by drop from a rather small height, the minimum height being just a little greater than the diameter of the drop formed, and the maximum height for this primary drop formation going up to 2 or 3 cm., depending upon the liquid and its dilution. The drop as it comes down does not coalesce with the liquid immediately on its impact with the surface but remains floating for a short time. If now the height from which the drops fall is raised above the said maximum height, there is a cessation of the phenomenon until the height has reached a certain minimum value for a particular liquid, when the swimming drops on the liquid surface again make their appearance. These drops are formed by splashes (Worthington's splashes) which cause them to be detached from the main body of the liquid when they float on its surface. These we term secondary drops. For any particular liquid, thus, there is a certain range of height during which there is no formation of drops at all.

* *Zeits. f. Phys.* Jan. 1927.

The primary drops have, as a rule, larger sizes than the secondary, while the life of the secondary drops is generally longer than that of the primary ones. The primary drops are also less mobile compared with the secondary ones.

The phenomenon can be easily demonstrated with the help of Boys's soap solution, or a solution of phenyle in water. The curves in fig. 1 (*a*) show the maximum and minimum heights for primary and secondary drop formation respectively when the liquid employed is Boys's soap solution of different strengths. Fig. 1 (*b*) shows similar curves for phenyle. 25 per cent. soap solution and 30 per cent. phenyle solution had the smallest range of no drop formation.

Fig. 1.



(a) percentage of Boys Soap solution (b) percentage of Phenyle.

Among other methods of such drop formation may be mentioned : (1) dipping a piece of cotton cloth in the liquid and holding it above the surface, this method being most suitable for fats and oils at high temperatures ; (2) vibrating (by bowing) the sides of the vessel holding the liquid, this method is most suitable for liquids of low surface-tension like ether, petrol, methylated spirit, turpentine, etc., and gives rise to secondary drops ; (3) water-drops can be easily made to float by allowing a spray of water to fall, horizontally or vertically, on a basin full of water.

A large number of liquids were studied and the results as regards drop formation can be classified as follows :—

(1) Light liquids of low surface-tension and low viscosity show the formation of secondary drops. They are not easily

amenable to the formation of primary drops. If any such drops are formed their life is exceedingly small. Thus ether, alcohol, methylated spirit, kerosene oil, petrol, turpentine, etc., readily show the formation of secondary drops either by the burette or by the vibrating vessel method. Water gives no primary drops at all and gives rise to secondary drops by the burette or the spray method, but not by the vibrating vessel method.

(2) Inorganic substances and their solutions and thick syrupy liquids do not show this phenomenon at all. Thus mercury, solutions of inorganic salts in water, inorganic acids and their water solutions, glycerine, saturated sugar solution, etc., form neither the primary nor the secondary drops.

(3) Fats and oils at high temperatures show the phenomenon remarkably well. At comparatively low temperatures the primary formation is shown better, while at higher temperatures the secondary phenomenon is better shown. Thus paraffin-wax at 90° C. formed good primary drops which by coalescing with each other gave rise to some of the largest drops observed, having a diameter of about 12 mm. At this temperature it formed no secondary drops. At 150° C. it could not form primary drops, but tiny secondary drops were readily formed, some of which lasted for nearly five minutes. As a rule, the smaller the size of the drops the longer their life.

(4) Solutions of soap (Boys's soap solution or sodium oleate) in water, of phenyle in water, and of creosole in carbolic acid show both the primary and the secondary phenomena, and are perhaps best suited for such a study. Of these liquids phenyle is perhaps the most preferable on account of its cheapness, no difficulty or complications in preparing the solutions, and easy formation of drops of comparatively long life. A 30 per cent solution of phenyle was found to be the best for the production of the primary drops and a 10 per cent. solution for the secondary drops. In the case of soap and creosole solutions as well, it was found that a smaller dilution is more suitable for primary drop formation and a greater dilution for the secondary phenomenon. The most suitable Boys's soap solution for the exhibition of these phenomena was a 15 per cent. one. With this solution drops as large as 12·4 mm. in diameter were obtained (by coalescence of several smaller drops and using a jet of 2·52 mm. diameter). It seems worth while mentioning that a 30 per cent. solution of phenyle was also found to be very suitable for easy production of bubbles and films of long life.

Several factors have to be borne in mind for easy production of the drops and prolonging their lives. Thus the surface of the liquid should be free from impurities like dust particles, etc. Impurities in the falling liquid itself make the formation of drops rather difficult and make them unstable. Impurities in the surrounding medium should also be avoided. Dusty air, for instance, does not favour the production of the phenomenon. This is very evident in the case of water drops, which are never formed until the surrounding air is free from dust and saturated with moisture. An electrically-charged rod brought near the drops makes them unstable, coalesce, and disappear quickly.

Temperature has different effects on different liquids. If the temperature of soap solution be raised, the formation of drops becomes almost impossible. In the case of water the formation of drops becomes easier at higher temperatures, but their size is decreased. With fats and oils a high temperature makes the formation of the drops very easy and also prolongs their life.

Movement of the drops on the surface prolongs their life. Thus the secondary drops, which are more mobile than the primary ones, have also the longer life of the two. Vibration or motion of the surface itself also tends to prolong the life of the drops. Thus the drops produced by the vibrating vessel method have a comparatively longer life. Also, if the drops are formed on the surface of a flowing stream of the liquid their life is prolonged.

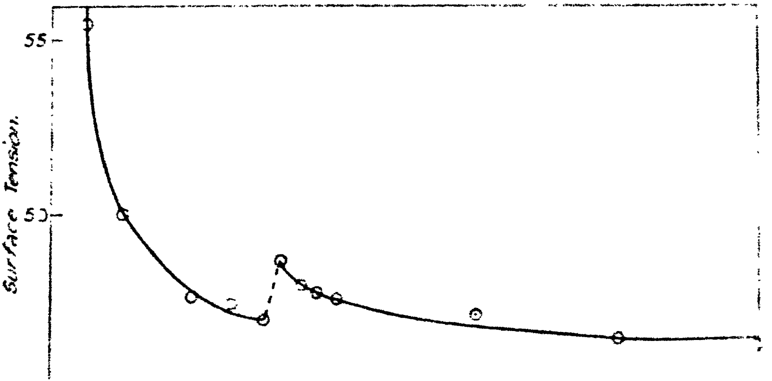
The life of the drops also becomes longer when the drops are formed inside an immiscible liquid. Thus water drops formed on a water surface covered with petrol or kerosene oil or olive oil (Darling's drops) have a fairly long life. The effect of the surrounding medium is evidently due to the cushions of the medium formed in between the drop and the liquid surface. The more viscous the surrounding medium, the stronger the layer which prevents the drop from combining or mixing with the main body of the liquid. Thus the more viscous the surrounding medium, the stabler the drops and the longer their life.

Addition of a more viscous liquid to the mother liquid stabilizes the drops and prolongs their life. Thus, in case of soap solution, the life of the drops is considerably increased by addition of glycerine, and the greater the amount of glycerine added, the longer lived the drops. Similarly, in case of ether drops (by the vibrating vessel method), their life is considerably increased by the addition of a small quantity of mustard oil to the liquid.

The size of the drop is increased by increasing the radius of the jet from which the drops issue when this particular method of drop formation is employed.

It would appear that the properties which play an important part in the production of this phenomenon are surface-tension, viscosity, and density of liquid. A detailed investigation to find the values of all these quantities for the principal liquids experimented on was, therefore, undertaken. As a result of this, it appeared that viscosity is mainly responsible for the stability and the long life of the drops, and the surface-tension mainly for their size. It also appeared that the liquids most suitable for the formation of primary drops (having long life, easy formation, and large size) should have a surface-tension ranging between 20 and 80 dynes per cm., a viscosity up to about ·25 c.g.s. unit, and a density in the neighbourhood of unity. For the secondary formation by the burette method, the surface-tension should range between 15 and 80, the viscosity up to ·046, and the density about unity; and for the secondary formation by the vibrating vessel method, surface-tension 15 to 30, viscosity up to ·010, and density smaller than unity.

Fig. 2.



While studying the surface-tensions a very interesting observation was made. In the case of phenyle solution, for instance, it was found that the surface-tension decreased as the amount of phenyle in the solution increased till the 30 per cent. stage was reached. At this point there was a small sudden rise of the surface-tension, when again it decreased but very slowly with the increase of phenyle in the solution. The surface-tension was determined by several methods, namely: by the rise in the capillary tube; by weighing the drops; by the method of ripples; and by Warren's surface-tension balance method [*]. Fig. 2 exhibits the type of results obtained. It may be remembered that the best solution for exhibition of primary drops by phenyle was a 30 per cent. one, and that at this concentration the range of no drop formation is also a minimum for this substance. In the case of Boys's soap solution the concentration surface-tension curve shows a similar dip for a 15 per cent. solution, and a solution of this strength is also the most suitable for drop formation.

These coincidences indicate that the depression in the curve has an important bearing on the easy formation of floating drops. A detailed study of changes of surface-tension in these regions for these two liquids, and measurements of surface-tension and viscosity of oils at different temperatures, will perhaps be of help in elucidating the phenomenon and is proposed to be undertaken at a subsequent date.

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XXVIII. *The Air-flow around a Circular Cylinder in the Region where the Boundary Layer separates from the surface.* By A. Fage, *A.R.C.Sc., of the Aerodynamics Department, The National Physics Laboratory* [†].

Introduction.

(1) IN some recent experiments on the measurement of the velocity distribution in the boundary layer along a smooth plane surface, J. M. Burgers [‡] and B. G. van der Hegge Zijnen have shown that the motion in the early part of the layer is laminar, and that a transition to the turbulent state begins at a critical value of $(V_0\delta/\nu)$, where δ is the thickness of the boundary layer, and V_0 and ν are the velocity and the coefficient of kinematic viscosity of the fluid. The

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[*] Phil. Mag., Aug. 1927.

[†] Communicated by E. F. Relf, A.R.C.Sc.

[‡] *Mededeeling*, Nos. 5 & 6. Laboratorium voor Aerodynamica en Hydrodynamica der Technische Hoogeschool te Delft.

critical value, which depends on the character of the turbulence initially existing in the fluid, was found to be about 3000 when the plate was mounted in a comparatively steady air-stream. It was also observed that the transition from the laminar to a turbulent state was accompanied by a marked opening-out of the boundary layer. There was, however, no apparent tendency for the layer to separate from the surface, which was aligned parallel to the direction of the undisturbed wind. To avoid ambiguity, it is necessary to mention here that the boundary layer is the narrow region in the immediate vicinity of the surface where the whole of the retarding influence due to the surface may be considered to operate; and that a flow is laminar when the speed and direction of motion at any point are independent of time, and turbulent when they change continually with time.

(2) It is a matter of common observation that when a surface is curved the boundary layer eventually separates from it; and this fact raises the interesting question as to whether the conditions in the layer around such a surface resemble those in the layer along a plane surface, and, if so, whether the phenomenon of separation is associated with the rapid opening-out of the boundary layer and the concomitant change from the laminar to a turbulent state of flow. To obtain information on this subject, a circular cylinder of large diameter was mounted in a wind tunnel and the boundary layer located from observations of total head taken close to the surface with an exceedingly small tube. The subsequent analysis will show that the distinctive traits of this curved boundary layer resemble those common to the layer along a plane surface; that there is a critical point on the cylinder; and that the separation of the layer from the curved surface occurs just beyond this critical point.

(3) There is a particular range of Reynolds's number—$VD/\nu = 10^5$ to $3{\cdot}5\times10^5$ approx., where D is the diameter—through which the character of the flow around a circular cylinder undergoes a marked change[*]. The drastic character of this change can be realized from the fact that the drag coefficient falls from 0·60 to 0·20 approx. over this range of (VD/ν). In view of the fact that the value of the investigation would be enhanced if these different types of flow (see fig. 9) were explored, it was decided to select a cylinder of large diameter, so that with the speed range available in the wind tunnel this particular range of (VD/ν) could be

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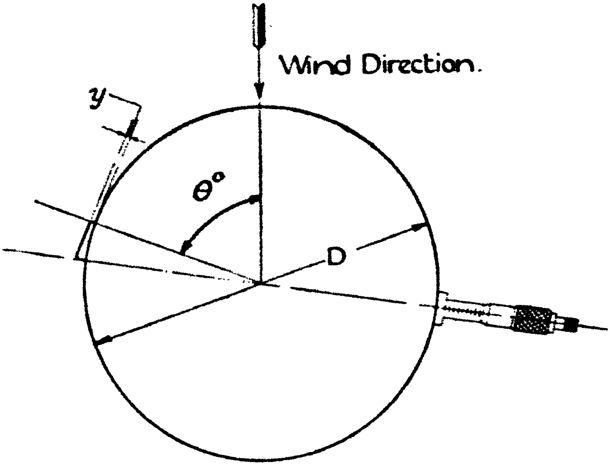
[*] Relf & Simmons, Phil. Mag., February 1925.

covered. The diameter chosen was 8·9 inches. It will be realized that a further advantage of the large diameter is that it favours increased accuracy of observation, since the thickness of the boundary layer, which is small in any case, is directly proportional to the diameter at a constant value of (VD/ν).

Description of Experiments.

(4) The cylinder was mounted between the floor and roof of a 4-foot wind tunnel. The observations taken were confined to the plane passing through the median section of the cylinder, where the flow can be regarded as two-dimensional. The experiments were designed to measure, at five wind speeds (22·0, 26·9, 39·2, 57·9, and 71·4 ft./sec.), radial distributions of total head near the surface. The method of experiment was to take, at each wind speed, with a very small tube (described later) observations of total head at known radial distances (y) from the surface as the cylinder was rotated by steps of 5° through an angular range extending from about 50° to 120°. The total-head distributions across radial lines were afterwards obtained by plotting these observations against y at a constant value of θ, where θ defines the position of the line measured from the direction of the undisturbed wind (see fig. 1). The minimum distance from the surface at which observations were taken was about

Fig. 1.



0·0037 inch, that is, when the tube touched the surface. The values of the total head at the surface (where the velocity is zero) were obtained directly from observations of pressure at a hole in the surface situated in front of, and some distance below, the small tube and beyond its influence. It was found at a later stage in the experiments that the observations (pressure and total head) taken near and beyond the region of maximum negative pressure were influenced by the presence of a micrometer head on the opposite side of the cylinder (see fig. 1). All the observations in the paper refer therefore to a cylinder with a micrometer head protruding from its surface. Further, the observations have not been corrected for the modification of the flow due to the constraint of the tunnel walls.

(5) *The Total-head Tube.*—Since the thickness of a boundary layer is, in general, very narrow, it was essential to use an exceedingly small total-head tube and to record its position relative to the surface with good accuracy. The tube was constructed from the finest hypodermic steel tube available (external diameter 0·0197 inch), pressed at the mouth into a rectangular form with the external dimensions 0·0074 inch by 0·021 inch approximately. The tube was mounted so that the longer side of the rectangular section was parallel to the axis of the cylinder. A microscopic examination showed that the opening in the mouth of the tube was irregular, but that the average width and height appeared to be about 0·0017 and 0·0053 inch respectively.

The small exploring total-head tube was soldered into a larger hypodermic steel tube, which passed through a small hole in the cylinder. This tube was moved radially by means of a micrometer screw mounted externally on the opposite side of the cylinder. The diagrammatic sketch of fig. 1 shows the method of mounting the total-head tube, and is self-explanatory. It should perhaps be mentioned that a suitable spring device was fitted within the cylinder to eliminate backlash between the sliding total-head tube and the rotating micrometer screw.

(6) It was at first intended that the position of the total-head tube should be measured directly on the micrometer scale. This method was, however, discarded because the datum reading involved contact of the tube with the surface and it was difficult to make sure that the tube, owing to its frailty, was not distorted. Moreover, the possibility of a deflexion of the supporting tube, due to a constraint at the

small hole in the cylinder through which this tube passed, could not be ignored.

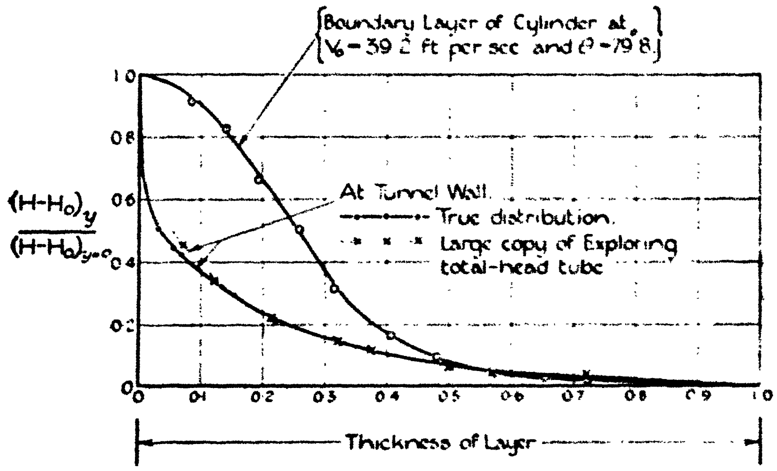
The method of measurement finally adopted was to illuminate the generator of the cylinder, which was in the radial plane passing through the mouth of the total-head tube, by means of a band of light projected from behind and normal to this radial plane, that is, tangential to the surface at the generator. The distance between this generator and the centre of the mouth of the tube was then measured by means of a travelling microscope with cross wires, mounted in front of the cylinder and focussed on the mouth of the tube. This method proved both simple and accurate in operation, and it was possible to measure the radial distance of the tube from the surface to within four ten-thousandths of an inch.

(7) *The Accuracy of the Total-head Observations.*—Experiments were also devised to obtain information on the general accuracy of the observations taken with the small total-head tube, and more especially to determine whether these observations would allow a reliable estimate to be made of the thickness (δ) of the boundary layer. The principal doubt concerning the accuracy of observation arises from the fact that the width of the tube is in some cases a large fraction of the width of the region of total-head gradient near the surface, so that the pressure measured may not correspond to the total head in the filament of air impinging on the geometric centre of the mouth of the tube. These subsidiary experiments will now be described.

(8) It is well known that in the vicinity of the wall of a wind tunnel there is a layer of air, of appreciable width, across which there exists a gradient of total head. At the working section of the tunnel the width of this layer was about 5·5 inches, that is, 100 times greater than the thickness of the boundary layer near the point on the cylinder where the pressure has its maximum negative value (see later). To obtain some idea of the accuracy of observation in the boundary layer at this region of the cylinder (where the thickness of the layer was only about 7·5 times greater than the external width of the tube), it was decided to compare the total-head distribution in the "wall" layer measured with a large copy of the small exploring tube to a scale of 100 : 1, with the true distribution obtained with a small total-head tube. The two curves of total head are given in fig. 2; and it is seen that they are in very close agreement, except

within the inner 15 per cent. of the width of the layer at the wall. Included in fig. 2 is a curve (taken from fig. 6) which may be regarded as representative of the total-head distribution across a section of the boundary layer of the cylinder near the point of maximum negative pressure. There are marked differences in the two distributions of total head, but in general, the gradient of total head in the boundary layer of the cylinder does not appear to be more severe than that in the "wall" layer. It follows, then, that the observations taken with the small exploring tube, although perhaps uncertain *very near* the surface (say within $0 \cdot 15\delta$), are reliable in the outer region of the boundary layer.

Fig. 2.

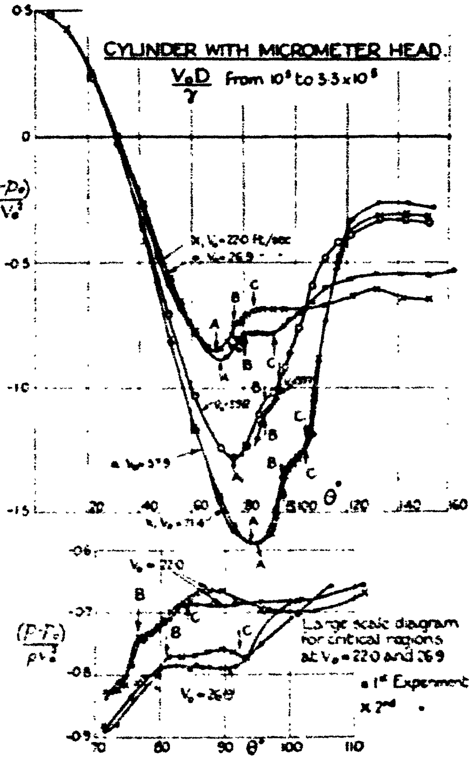


(9) To determine to what extent the smallness of the exploring tube would influence observations taken in a uniform stream, a comparison was made with observations taken with a much larger tube under corresponding conditions. It was found that over the speed range covered (15 to 80 ft./sec.) the scale effect was too small to be detected with any accuracy. It is of interest to mention that a confirmation of this result was obtained from the experiments with the cylinder, for it was found that the total head observed with the small tube just outside the boundary layer was equal, except occasionally at the lowest speed, to that measured with a much larger tube in the undisturbed stream.

Discussion of the Observations.

(10) *Pressure Observations.*—The distributions of pressure around the surface of the cylinder (with micrometer head), at the five wind speeds (V_0) of experiment, are given in fig. 3. The commonly accepted method of plotting, namely $(p-p_0)/\rho V_0^2$ against θ has been adopted, where p is the

Fig. 3.



pressure at a point on the surface given by θ (see fig. 1), and p_0 and V_0 are the pressure and the velocity respectively in the undisturbed stream. These curves exhibit very clearly the marked changes in the pressure distribution which occur over the selected range of VD/ν (10^5 to $3\cdot3\times10^5$). The drastic character of these changes also manifests itself in the drag coefficient (k_D) which, as shown in Table I., falls from 0·63 to 0·22 over the same range of (VD/ν). It will be observed that the coefficient of the maximum negative pressure increases with the wind speed, and also that there is a progressive displacement of the point at which this pressure occurs towards the back of the cylinder. The maximum negative pressure measured at the higher wind speeds 57·9 and 71·4 ft./sec. were $-1{\cdot}62\,\rho V_0^2$ and $-1{\cdot}63\,\rho V_0^2$ respectively. It should perhaps be mentioned that these values were greater numerically than the corresponding values for the naked cylinder, which were $-1{\cdot}43\,\rho V_0^2$ and $-1{\cdot}46\,\rho V_0^2$ respectively; and that these latter values are lower than the theoretical value $(-1{\cdot}62\,\rho V^2)$ predicted for an 8·9-inch cylinder in an inviscid stream in a 4-foot tunnel.

TABLE I.

Cylinder in a 4-foot Tunnel. (With micrometer head removed.)

V_0 ft. per sec.	$\left(\frac{V_0 D}{\nu}\right)$.	Drag coefficient k_D.
22·0	102,600	0·634
26·9	125,400	0·511
39·2	182,800	0·227
57·9	270,000	0·192
71·4	333,000	0·218

(11) An important trait exhibited in each of the curves of fig. 3 is the pronounced inflexion (marked BC) between the point of maximum negative pressure (marked A) and the region where the pressure is almost constant. The principal purpose of the subsequent analysis will be to show that the change from the laminar to a turbulent state of flow in the boundary layer probably occurs in this region BC, and that the layer has completely separated from the surface at the point C.

(12) *Total-head Observations.*—The total head (H) at a point situated a radial distance (y) from the surface was measured with the small exploring tube against the datum total head (H_0) in the undisturbed stream. These observations, reduced to the non-dimensional form $(H-H_0)/\rho V_0^2$, are plotted against $(1000y/D)$ in figs. 4–8 (a). The total

head at the surface ($y = 0$) was not measured directly, but was determined from the observations of pressure $(p-p_0)$ by the relation $(H - H_0) = (p-p_0) - 0{\cdot}5\,\rho V_0^2$; these values are

Fig. 4.

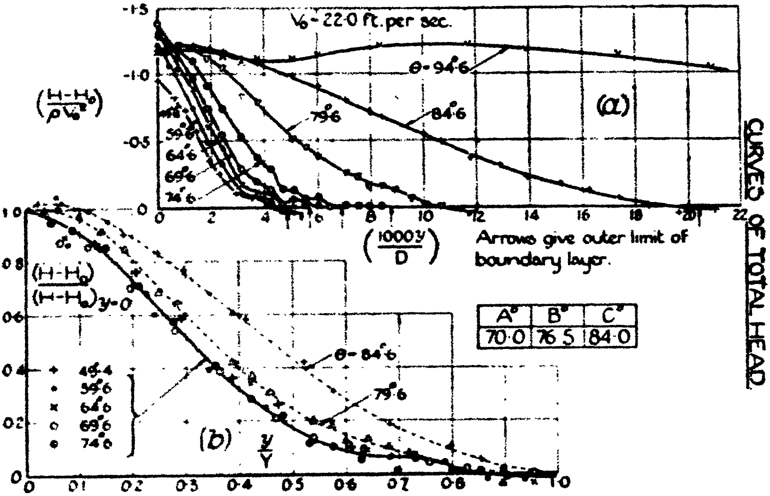
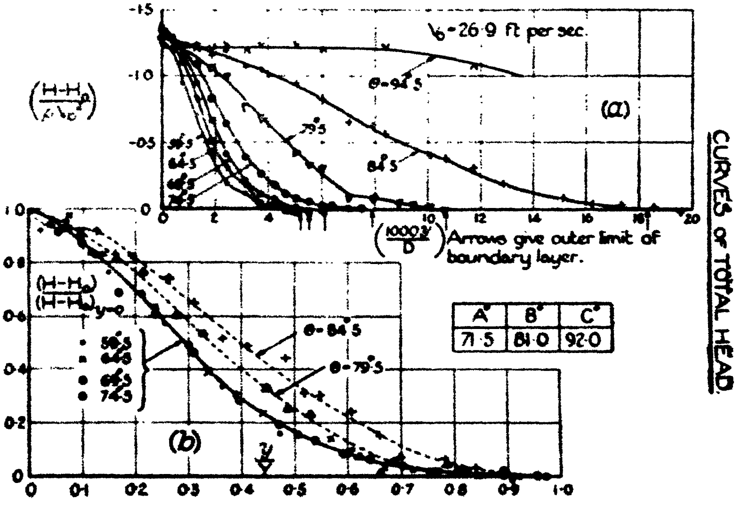


Fig. 5.



also plotted in figs. 4–8 (*a*). It is considered to be a matter of some importance that the estimated values of $(H-H_0)/\rho V_0^2$ at $y = 0$ support the tendencies indicated by the curves drawn through the observations taken with the tube.

In view of the fact that other workers may desire to use the experimental observations of total head given in figs. 4–8 (*a*), those taken at the extreme speeds of experiment

Fig. 6.

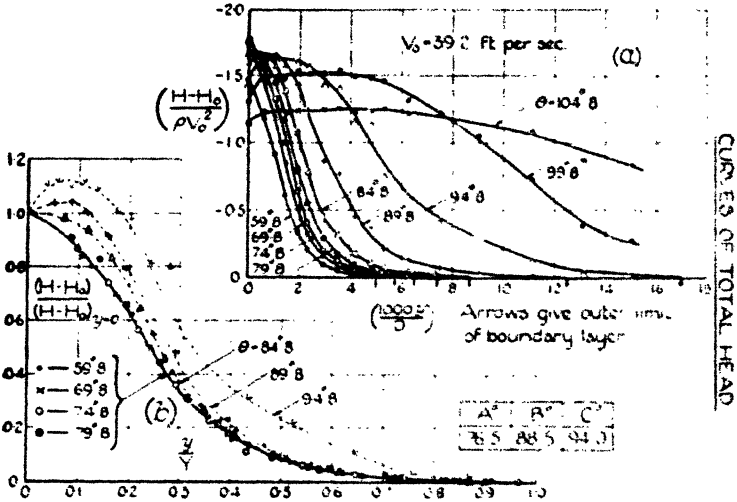
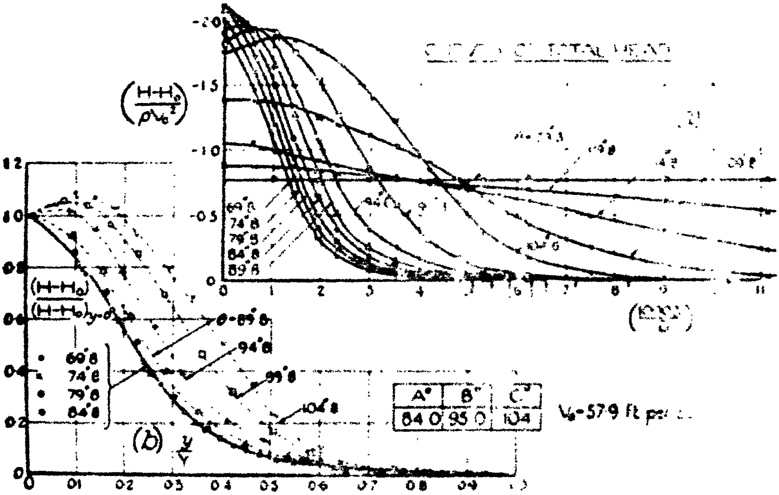


Fig. 7.



(22·0 and 71·4 ft. per sec.) are given in Tables II. and III., as well as in figs. 4 and 8 (*a*). The observations for the intermediate speeds are presented only in figs. 5–7.

TABLE II.

Values of $(\mathrm{H}-\mathrm{H}_0)/\rho \mathrm{V}_0^2$ for $\mathrm{V}_0 = 71\cdot4$ ft. per sec.
Value of θ° given at top of each column.

$\frac{1000y}{\mathrm{D}}$.	49·8	59·8	69·8	74·8	79·8	84·8	89·8	94·8	99·8	104·8	109·8	114·8	119·8	129·8
0	−1·257	−1·595	1·888	−2·010	−2·091	−2·121	−2·102	−1·973	−1·8[illegible]2	−1·732	−1·421	−1·096	−0·925	...
0·623	−0·816	−1·134	1·430	−1·555	−1·670	−1·780	−1·860	−1·925	−1·930	−1·873	−1·330	−1·024	−0·919	−0·796
1·035	−0·462	−0·695	−0·940	−1·080	−1·225	−1·378	−1·531	−1·695	−1·830	−1·820	−1·254	−0·945	−0·859	0·788
1·424	−0·225	−0·363	−0·550	−0·651	0·794	−0·945	−1·120	−1·363	−1·655	−1·761	−1·175	−0·884	−0·834	−0·792
1·902	0·097	0·160	0·258	−0·325	−0·408	−0·518	−0·683	−0·935	−1·345	−1·627	−1·058	−0·833	−0·813	−0·796
2·331	−0·048	−0·081	−0·137	−0·173	−0·222	−0·285	−0·400	−0·603	−1·030	−1·440	−0·995	−0·806	−0·802	−0·799
2·992	−0·022	−0·045	−0·060	0·077	−0·102	−0·134	−0·187	0·290	−0·585	−1·059	−0·849	−0·739	−0·764	−0·790
3·522	−0·014	−0·026	−0·039	−0·055	−0·067	−0·080	−0·110	−0·156	−0·267	−0·803	−0·759	−0·715	−0·759	−0·800
4·195	−0·001	−0·011	−0·018	−0·025	−0·031	−0·039	−0·056	−0·095	−0·181	−0·484	−0·608	−0·652	−0·732	−0·804
4·820	−0·001	−0·006	−0·011	0·016	−0·021	−0·026	−0·030	−0·053	−0·102	−0·282	−0·483	−0·589	−0·695	−0·790
5·302	...	0	−0·010	−0·011	−0·011	−0·017	−0·023	−0·031	−0·061	−0·180	−0·379	−0·551	−0·680	−0·800
6·240	...	...	−0·006	−0·007	−0·006	−0·009	−0·014	−0·021	−0·061	−0·079	−0·241	−0·456	−0·630	−0·774
7·51	...	...	...	..	...	...	+0·014	+0·011	−0·006	−0·025	−0·134	−0·367	...	...
9·04	...	...	...	...	..	...	...	...	−0·006	−0·009	−0·065	−0·261	−0·512	−0·780
11·12	...	...	...	...	...	...	...	...	...	−0·008	−0·018	−0·151	−0·412	−0·775
13·13	...	...	...	...	..	...	.	...	...	...	−0·006	−0·070	−0·344	−0·775
15·05	...	...	..	...	...	...	...	...	...	...	0	−0·025	−0·229	−0·754

Fig. 8.

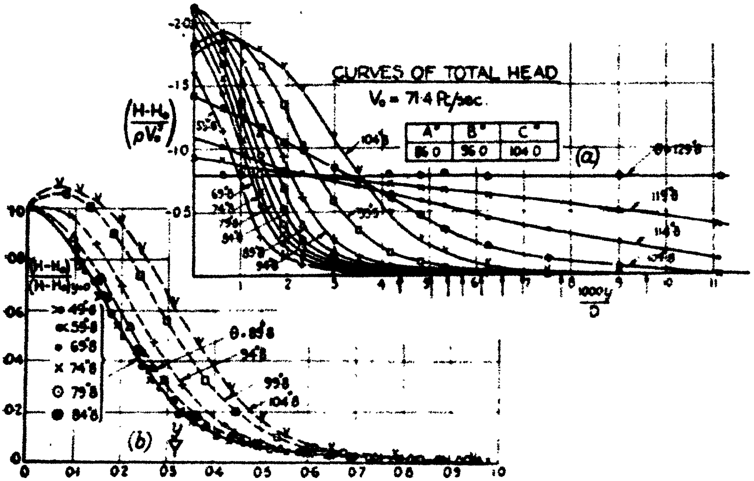


TABLE III.

Values of $(H - H_0)/\rho V_0^2$ for $V_0 = 22·0$ ft. per sec. Value of θ° given at top of each column.

1000y/D.	59·6	64·6	69·6	74·6	79·6	84·6	94·6	1000y/D.	49·4
0	−1·230	−1·300	−1·340	−1·290	−1·220	−1·180	−1·180	0	−0·953
0·429	−1·060	−1·165	−1·222	−1·223	−1·200	−1·208	−1·175	0·623	−0·826
0·774	−1·041	−1·120	−1·194	−1·189	−1·220	−1·147	−1·083	1·035	−0·735
1·318	−0·743	−0·895	−0·978	−1·100	−1·195	−1·208	−1·183	1·424	−0·567
1·861	−0·487	−0·609	−0·750	−0·919	−1·119	−1·188	−1·160	1·902	−0·349
2·438	−0·324	−0·447	−0·545	−0·750	−1·042	−1·172	−1·142	2·351	−0·253
3·138	−0·108	−0·166	−0·294	−0·533	−0·839	−1·118	−1·107	2·992	−0·102
3·714	−0·090	−0·119	−0·195	−0·370	−0·796	−1·070	−1·100	3·522	−0·078
4·250	−0·055	−0·102	−0·137	−0·289	...	...	...	4·195	−0·012
4·672	+0·003	−0·005	−0·020	−0·131	...	...	...	4·820	+0·012
5·070	+0·003	−0·008	−0·061	−0·136	−0·516	−0·984	−1·100	5·302	+0·018
5·540	...	+0·050	−0·032	−0·067	−0·457	...	...	...	...
6·010	+0·003	+0·003	−0·020	−0·078	−0·382	−0·908	−1·130	...	...
6·42	...	+0·010	−0·008	−0·008	...	...	...	...	...
7·04	...	+0·012	+0·009	−0·014	−0·248	−0·804	...	...	...
7·51	...	...	−0·002	−0·014	−0·230	...	...	...	...
7·94	...	...	+0·009	+0·004	−0·154	−0·721	...	...	...
8·40	...	...		0·002	−0·160	−0·692	−1·209	...	...
8·93	...	...	...	...	−0·125	...	...	...	...
9·51	...	...	...		−0·078	...	...	...	...
10·06	...	...	...		−0·020	−0·545	...	...	...
10·63	...	...	...		−0·008	−0·499	...		...
11·75	...	...	...	...	+0·050	−0·370	−1·200	...	...

(13) There are prominent features common to the total-head curves taken at each wind speed, V_0. A study of these features will now be made; and especially of those which are related to the flow around that part of the cylinder previously designated ABC, and characterized by a marked inflexion in the curve of the pressure distribution (see fig. 3). For convenience of reference, the values of θ at each of the points A, B, and C are given in figs. 4–8. Also, to indicate more readily the changes in the character of the total-head distribution at the several radial sections prior to the point C on the cylinder, a second series of curves (*b*) is included in each of the figs. 4–8. These curves (*b*) are obtained by plotting the ratio $(H-H_0)_y/(H-H_0)_{y=0}$ against (y/Y), where Y represents the value of y at the point where the total head just reaches the value (H_0) in the undisturbed stream. It will be noted that if the local air-stream has not separated from the surface, the value of Y is equal to the thickness (δ) of the boundary layer.

(14) The method of plotting adopted in figs. 4–8 (*b*) shows that the observations taken in a relatively large part of the boundary layer situated forward of the point (A), of maximum negative pressure,—the angular range covered varies from 25° for $V_0=22{\cdot}0$ to 35° for $V_0=71{\cdot}4$—lie on a common curve within the accuracy of experimental observation. In other words, the opening-out of the boundary layer and the fall of pressure around the surface do not influence (over this region) the character of the total-head distribution across a radial section. There is, however, a progressive change in the distribution, especially near the surface, as the position of the section is taken beyond the point A.

(15) It is to be expected that in the immediate vicinity of the point where the layer begins to separate from the surface the total head would change very slowly with the radial distance from the surface, that is, $\partial(H-H_0)/\partial y$ should tend to a zero value as y approaches its zero value; and also that when the "breakaway" was completed, the total head should remain constant over a relatively large radial distance from the surface. It should therefore be possible to obtain from the curves in figs. 4–8 (*a*) and (*b*) indications of the positions where the flow begins to leave the surface and where the separation is completed. This information is collected in Table IV. together with the values of θ defining the positions of the points B and C. The values of θ given in the columns 3 and 4 of the table are

only approximate, and refer to the curves which most closely fulfil a desired condition.

Table IV. reveals two important facts: firstly, that the boundary layer begins to leave the surface at the point B, since the value of $\partial(H-H_0)/\partial y$ is zero near this point; and secondly, that the separation appears to be completed at the point C. The flow in the region BC is therefore of a peculiar character, and that this is so is further indicated by the conspicuous "humps" in the total-head curves, exhibited near the surface at all speeds except 26·9 ft./sec. It is perhaps of interest to mention that since the tube was always pointing in the same tangential direction the "humps" in the total-head curve can be accounted for on the assumption of a reversal in the direction of flow.

TABLE IV.

V_0 ft./sec.	Value of $\theta°$ at point B. (Fig. 3.)	Value of $\theta°$ where $\frac{\partial(H-H_0)}{\partial y}=0$. (Figs. 4–8 (b).)	Value of $\theta°$ where the separation appears to be completed. (Figs. 4–8 (a) & (b).)	Value of $\theta°$ at point C. (Fig. 3.)
22·0	76·5	Near 79·6	Near 84·6	84·0
26·9	81·0	Not clear, say 84·5	94·5	92·0
39·2	88·5	Between 84·8 & 89·8	Near 94·8	94·0
57·9	95·0	Near 94·8	Near 104·8	105·0
71·4	96·0	Near 94·8	Near 104·8	105·0

(16) *Vortex Sheets.*—It should be possible to obtain an idea of the position of the region where the boundary layer separates from the surface from a pattern of the flow around the cylinder, or, better still, from the vortex sheets trailing behind the cylinder, since these sheets originate in the boundary layer. To locate the position of these sheets, observations of total head were taken across several lateral sections of the wake, with a tube which could be directed into the local stream. The nature of the total-head curves so obtained is illustrated in fig. 3 of an earlier paper dealing with the structure of vortex sheets *. The method of determining the position of points on the outer and inner

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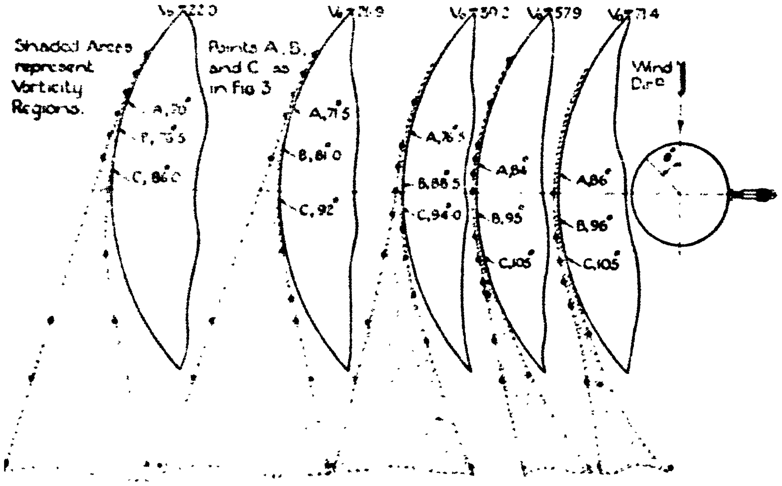
* Fage & Johansen, Phil. Mag. p. 421 (February 1928).

boundaries of a sheet is also described in the same paper. Briefly stated, a point on an outer boundary marks the position beyond which the total head is constant and equal to the value (H_0) in the undisturbed stream, and a point on an inner boundary where the total head has fallen to a minimum value. It should be added that the points on the outer and inner boundaries close behind a separation region were not taken from curves obtained from lateral explorations, but from the appropriate curves of figs. 4–8 (*a*), and also from some observations (not included in the paper) taken with a small exploring tube attached to the cylinder.

Fig. 9.



(17) The shape and position of the vorticity sheets trailing behind the cylinder, at each speed, are shown by the shaded areas in fig. 9. A retrograde movement of the separation region, and a more gradual separation of a vortex sheet from the surface, as the speed is progressively increased are clearly indicated; and the general impression created is that the flow is more conformable to the surface at the higher wind speeds. It is also seen that the formation of a marked dead-air region behind the cylinder commences almost immediately after the point C (BC is the separation region) at the lower speeds 22·0 and 26·9 ft./sec., but that this does not appear to be the case at the higher speeds 57·9 and 71·4 ft./sec. It does not, however, necessarily follow from the delay in the formation of a marked dead-air region at

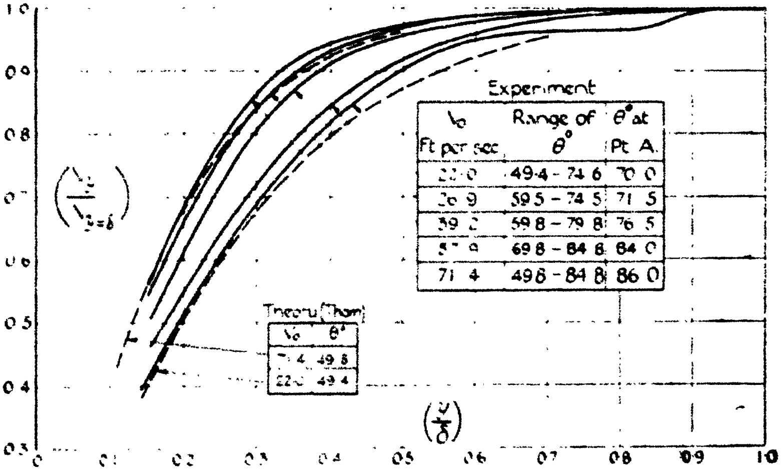
these higher speeds that the separation of the boundary layer is not completed at the point C; for the layer after leaving the surface becomes a vortex sheet and opens out by the inflow of air across its boundaries, in a manner dependent on the general configuration of the neighbouring flow; and it may well be that the inner boundary of the sheet follows closely the contour of the surface, so that there is a very narrow band of "dead air" between the sheet and the surface. A study of the total-head curves taken at these higher speeds at the sections beyond the point C gives support to this point of view.

(18) *Velocity Distribution.*—If it be assumed that the pressure across a section of the boundary layer is uniform and equal to that measured at the surface, it follows that

$$\left[\frac{V_y}{V_{y=\delta}}\right]^2 = \left[1 - \frac{(H_0-H)_y}{(H_0-H)_{y=0}}\right]$$

within the layer. The value of the velocity (V_y) expressed as a fraction of the maximum velocity ($V_{y=\delta}$) can therefore be directly estimated when the corresponding value of $\left[\frac{(H_0-H)_y}{(H_0-H)_{y=0}}\right]$ is known. Further, figs. 4–8 (*b*) have shown that values of $\frac{(H_0-H)_y}{(H_0-H)_{y=0}}$ taken in the boundary layer extending some distance in front (the average range taken is about 20°) of the point A of maximum negative pressure fall very closely on a smooth curve when they are plotted against (y/δ). Values of $(V_y/V_{y=\delta})$ for this part of the boundary layer were therefore estimated from the above relation by the substitution of mean values of $\frac{(H_0-H)_y}{(H_0-H)_{y=0}}$ taken from the smooth curves of figs. 4–8 (*b*). The results are given by the full lines in fig. 10. No values of $(V_y/V_{y=\delta})$ for points very near the surface (that is, within $0{\cdot}15\delta$) are included because, as shown in § 8, the total-head observations in this region may be uncertain, and also because the predicted velocity is susceptible to small errors in $\frac{(H_0-H)_y}{(H_0-H)_{y=0}}$ as its value approaches unity. The curves in fig. 10 show that (over a range of $\theta°$ taken) the character of the velocity distribution across a section of the boundary layer taken at and prior to the point A changes consistently with the wind speed. Included in fig. 10 are two dotted curves showing for the extreme speeds ($V_0 = 22$ and 71·4 ft. per sec.) the theoretical distributions of velocity across a section of the boundary layer at $\theta = 50°$ approx. These theoretical curves, which were obtained from Dr. Thom's solution* of the simplified boundary layer equations for the laminar flow around the front part of a circular cylinder, indicate a scale effect on the velocity distribution of the same character as that obtained from experiment. Further, the good agreement between the theoretical and experimental curves (the agreement is much closer when the comparison is made with the actual experimental curves at $\theta = 50°$ instead of the mean

Fig. 10.



Experiment

V_0 Ft per sec	Range of $\theta°$	$\theta°$ at Pt A.
22·0	49·4 - 74·6	70·0
30·9	59·5 - 74·5	71·5
39·2	59·8 - 79·8	76·5
57·9	69·8 - 84·8	84·0
71·4	49·8 - 84·8	86·0

Theory (Thom)

V_0	$\theta°$
71·4	49·8
22·0	49·4

curves given in the figure) shows that the motion in the boundary layer at $\theta = 50°$ is laminar. Unfortunately, Dr. Thom's solution is not applicable in the region of maximum negative pressure, so that it is not possible to determine from a comparison with theory how far beyond $\theta = 50°$ the laminar motion persists. Further evidence on this subject can, however, be obtained from the work described in the following section.

Attention is directed to the peculiar shape of the outer part of the velocity curve taken at the lowest wind speed, 22 ft./sec., and it is tentatively suggested that this is connected with the relatively large disturbances in the general stream at this speed.

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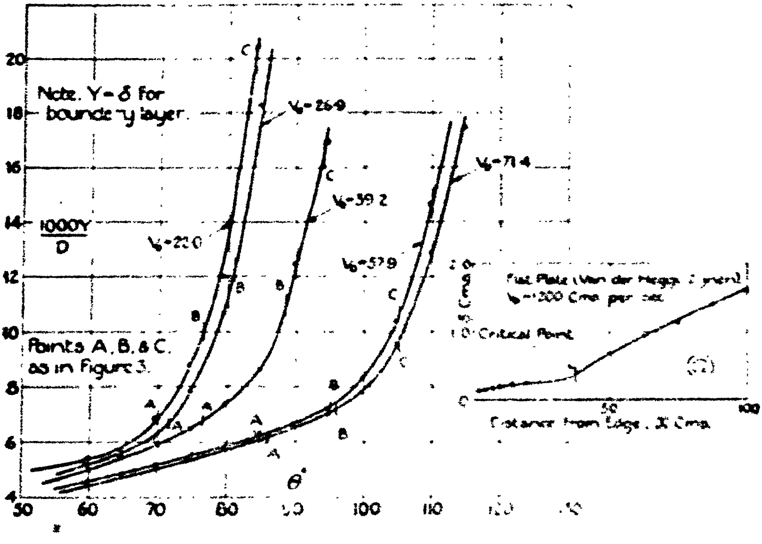
* Aeronautical Research Committee, R. & M. 1176.

(19) *The Thickness of the Boundary Layer.*—B. G. van der Hegge Zijnen * has shown that the transition from the laminar to a turbulent state of flow in the boundary layer along a smooth plane surface manifests itself by a marked increase in the thickness of the layer. If this be an essential phenomenon accompanying a transition, an indication of the position of the transitional region on a cylinder (provided such a region exists) should be obtainable from a curve giving the variation of the thickness of the boundary layer with the angular distance around the cylinder. Also it is to be expected that the flow in the boundary layer around the cylinder does change, for it has been shown that the flow in the early stages is laminar and, it may be presumed, turbulent after the layer has separated from the surface (point C). The manner in which the boundary layer around the cylinder opens out is shown in the early part of the curves of fig. 11, where values of (1000 Y)/D are plotted against θ. The values of Y (Y is defined in § 13) were determined directly from curves similar to those given in figs. 4–8 (*a*), but plotted

Fig. 11.



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* *Loc. cit.*

on a larger scale. Further, it follows from the definition of the term "boundary layer" that the value of Y gives the thickness (δ) of the layer prior to its separation from the surface.

The curves of fig. 11 show that up to the point A there is a steady increase in the value of Y (δ for the boundary layer) with the angular distance around the cylinder; and also that the point B is situated near to the point where the rapid opening-out of the boundary layer begins. An inflexion similar to that at the point B was observed by van der Hegge Zijnen in the corresponding (δ, x) curves for the boundary layer along a plane surface (see fig. 11 (*a*)); and he established, on evidence derived from the distributions of velocity across suitably-chosen sections, that the transition from the laminar to a turbulent state of flow began at the critical point where the rapid opening-out of the boundary layer occurred. A similar transition appears to take place in the case of the cylinder, for it has been shown that the motion in the boundary layer at some distance anterior to the point A (maximum negative pressure) is laminar (this would, of course, be expected unless the initial disturbances in the general stream are exceptional); and it would appear justifiable to assume that the flow at the point C is turbulent, since at this point the separation from the surface is completed.

Critical Values.

(20) The evidence obtained from the pressure curves of fig. 3, the total-head curves of figs. 4–8, and the (δ, θ) curves of fig. 11 lead to the conclusion that the flow in the boundary layer around the cylinder is critical at (or near) the point B. A special significance is therefore attached to the values of Reynolds's numbers ($V_0\delta/\nu$) and $(V_{y=\delta}) \cdot \delta/\nu$ at this point. These values, computed for the five speeds, are collected in Table V. It should be added that an average value of the coefficient of kinematic viscosity (ν), namely that for the standard atmosphere of pressure 760 mm. and temperature 15·6° C., has been taken in the computation, and also that the value of $V_{y=\delta}$ at the outer limit of the boundary layer was determined on the assumption made in § 18 from the relation

$$\left[\frac{V_{y=\delta}}{V_0}\right]^2 = 1 + \frac{2(p_0 - p)}{\rho V_0^2},$$

where p is the pressure at the point B.

It will be observed in Table V. that the values of ($V_0\delta/\nu$) (there is a slight irregularity at $V_0 = 57{\cdot}9$ ft./sec.) and

$(V_{y=\delta}) \cdot \delta/\nu$ show a marked progressive increase with the mean speed, V_0.

It is necessary, if the correct interpretation of the results in Table V. is to be made, to bear in mind that they were obtained with the cylinder mounted in an artificial wind stream, so that an increase of the wind speed, V_0, probably involves a change in the "scale" of the turbulence initially in the stream. The importance of this initial turbulence has been demonstrated by van der Hegge Zijnen, who found that a change of turbulence in the general stream, due to the introduction of a screen, reduced the critical value of $(V_0\delta/\nu)$ for the plane surface from 3000 to 1600, even although the relative mean speed was unchanged. It is therefore not irrelevant to mention that an impression was formed as the experiments with the cylinder proceeded, that the general stream was relatively more disturbed at the lower speeds—see the appropriate curves of total head and velocity near $(y = \delta)$.—and this may *partially* account for the lower values of Reynolds's numbers measured at these speeds.

Table V.

V_0 ft./sec.	At point B.					
	$\theta°$.	$\frac{\delta}{D}$.	$\frac{V_0\delta}{\nu}$.	$\frac{(p_0-p)}{\rho V_0^2}$.	$\left(\frac{V_{y=\delta}}{V_0}\right)$.	$\frac{\delta}{\nu}(V_{y=\delta})$.
22·0	76·5	0·0100	1030	0·74	1·57	1620
28·9	81·0	0·0122	1530	0·78	1·60	2450
39·2	88·5	0·0110	2010	1·05	1·76	3540
57·9	95·0	0·0073	1970	1·37	1·93	3800
71·4	96·0	0·0072	2400	1·38	1·94	4650

It is a noteworthy fact that the average values of $(V_0\delta/\nu)$ and $(V_{y=\delta}) \cdot \delta/\nu$ for the cylinder—they are 1790 and 3210 respectively—are of the same order of magnitude as the average value (3150) determined by van der Hegge Zijnen for the flat plate, and as the value (2300, lower critical) determined from the critical value for the flow in pipes, on the assumption that the radius of the pipe is equivalent to the thickness of the boundary layer, and the velocity at the axis is equivalent to V_0.

Summary.

(21) An examination of the air-flow round a circular cylinder in the region where the boundary layer separates from the surface has been made from observations of total head taken with an exceedingly small tube. The diameter of the cylinder and the range of wind speed selected were such as to allow markedly different types of flow to be considered. The analysis indicates that there is a critical point on the cylinder where a transition from the laminar to a turbulent state of flow in the boundary layer begins. The transitional region is marked by a rapid opening-out of the boundary layer. The critical value of Reynolds's number for the boundary layer progressively increases with wind speed over the range taken in the experiments. The average of these critical values for the cylinder is of the same order of magnitude as the average value by van der Hegge Zijnen for a plane surface. The separation of the boundary layer from the surface occurs just beyond the critical point.

(22) In conclusion, the writer wishes to acknowledge his great indebtedness to Mr. J. H. Warsap, who took most of the experimental observations in the paper, and also to Mr. A. Monk, who made the small total-head tube.

XXIX. *Note on a Geometrical Radiation Problem.*

By E. A. Milne, *F.R.S.*[*]

1. Dr. L. F. Richardson's recent interesting paper[†] on the radiation transmitted through a pair of parallel square apertures suggests that it may be worth while to publish the solution of the similar problem for a pair of circular apertures. Professor A. V. Hill two years ago required the solution of this problem for practical application to the case of a thermocouple receiver of circular section exposed to radiation through a parallel circular aperture, and asked me to investigate it. The problem happens to be one in which the necessary integrations can be effected in finite terms.

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[*] Communicated by the Author.

[†] Phil. Mag. [7] vi. p. 1019 (Nov. 1928).

2. Let a, b be the radii of two circular apertures whose planes are perpendicular to the line joining their centres. Let l be their distance apart. Let P, P′ be any two points in the two apertures respectively, (r, θ), (r', θ') their plane-polar coordinates with reference to origins at the centres of the apertures.

Let I be the intensity of radiation, supposed uniform, at any point of one of the apertures. Then the amount R of radiant energy passing through the first aperture and reaching the other aperture is, per second,

$$I\iiiint\frac{\cos^2\psi\, dS\, dS'}{PP'^2},$$

where ψ is the angle between PP′ and the normal at P or P′, and dS, dS' are elements of area.

Now $$\cos\psi = l/PP'$$

and $$PP'^2 = l^2+r^2+r'^2-2rr'\cos(\theta-\theta').$$

Hence

$$R = Il^2\int_{r=0}^{r=a}\int_{r'=0}^{r'=b}\int_{\theta=0}^{\theta=2\pi}\int_{\theta'=0}^{\theta'=2\pi}\frac{rr'\,dr\,dr'\,d\theta\,d\theta'}{[l^2+r^2+r'^2-2rr'\cos(\theta-\theta')]^2}. \quad . \quad . \quad . \quad (1)$$

But

$$\int_{\theta=0}^{\theta=2\pi}\int_{\theta'=0}^{\theta'=2\pi}\frac{d\theta\, d\theta'}{[A-B\cos(\theta-\theta')]^2} = \int_0^{2\pi} d\theta\int_0^{2\pi}\frac{d\phi}{[A-B\cos\phi]^2}$$

$$= 4\pi^2\frac{A}{(A^2-B^2)^{3/2}}$$

if $$|A| > |B|,$$

whence

$$R = 4\pi^2 I l^2\int_{r=0}^{r=a}\int_{r'=0}^{r'=b}\frac{(l^2+r^2+r'^2)\,rr'\,dr\,dr'}{[(l^2+r^2+r'^2)^2-4r^2r'^2]^{3/2}}.$$

In this put

$$r^2 = x, \qquad r'^2 = y.$$

Then

$$R = \pi^2 l^2 I\int_0^{a^2}\int_0^{b^2}\frac{(l^2+x+y)\,dx\,dy}{[(l^2+x+y)^2-4xy]^{3/2}}.$$

Next* put

$$l^2+x-y = \xi.$$

Then

$$R = \pi^2 l^2 I\int_0^{b^2} dy\int_{l^2-y}^{l^2+a^2-y}\frac{\xi+2y}{[\xi^2+4l^2y]^{3/2}}\,d\xi.$$

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* I am indebted to Prof. L. J. Mordell for pointing out to me that the ensuing integrations are quite practicable.

The integration with respect to ξ is readily performed, and we obtain

$$R = \frac{\pi^2 I}{2} \int_0^{b^2} \left[\frac{a^2-l^2-y}{\{((l^2+a^2-y)^2+4l^2y\}^{1/2}} + 1 \right] dy.$$

The last integration is effected by the substitution

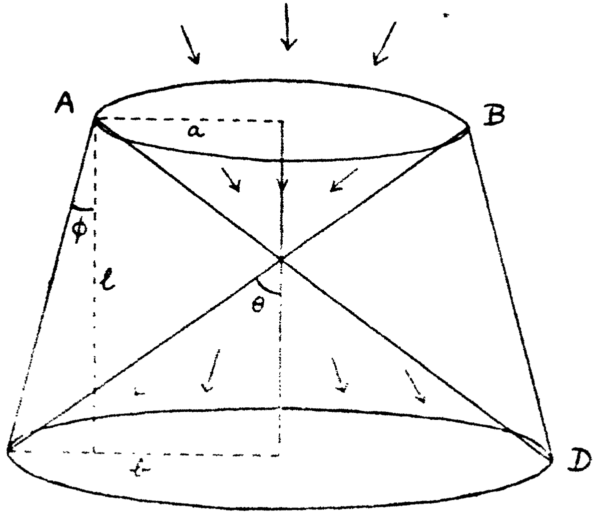
$$a^2-l^2-y=\eta,$$

whence we find finally

$$R = \tfrac{1}{2}\pi^2 I\left[a^2+b^2+l^2-\left[(a^2+b^2+l^2)^2-4a^2b^2\right]^{1/2}\right]. \quad (2)$$

This formula may be checked by noticing that, as $l \to 0$, R must tend to $\pi I . \pi c^2$, where c is the smaller of a and b;

Fig. 1.



and that, as $l \to \infty$, $R \sim \pi^2 a^2 b^2 I/l^2 = I . \pi a^2 . \pi b^2/l^2 =$ Intensity × area × small solid angle.

3. Professor A. V. Hill pointed out to me that, when $a=b$, the expression (2) can be given a simple trigonometrical form. The following is an extension of Hill's result to the general case.

Assume (without loss of generality) $b > a$, and put

$$\tan\theta = \frac{a+b}{l}, \qquad \tan\phi = \frac{b-a}{l}.$$

The angles θ and ϕ thus defined have the geometrical meanings indicated in fig. 1. All radiation incident on AB at an angle of incidence less than ϕ reaches CD; no radiation incident on AB at an angle of incidence greater than θ reaches CD. Simple transformations then show that (2) reduces to

$$R = \tfrac{1}{4}\pi^2 l^2 I(\sec\theta - \sec\phi)^2. \quad . \quad . \quad . \quad . \quad (3)$$

If the screen containing the aperture AB were removed, the radiation falling on CD would be

$$\pi b^2 \,.\, \pi I = \tfrac{1}{4}\pi^2 l^2 I\,(\tan\theta + \tan\phi)^2.$$

Hence the fractional reduction caused by the aperture is

$$\left(\frac{\sec\theta - \sec\phi}{\tan\theta + \tan\phi}\right)^2 = \left[\frac{\sin\frac{1}{2}(\theta-\phi)}{\cos\frac{1}{2}(\theta+\phi)}\right]^2. \quad . \quad . \quad (4)$$

Similarly, if the radiation is incident on CD, the fractional reduction in the amount reaching AB caused by the screen containing CD is

$$\left[\frac{\sin\frac{1}{2}(\theta+\phi)}{\cos\frac{1}{2}(\theta-\phi)}\right]^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When the apertures are equal, $\phi = 0$, and (4) and (5) reduce to $\tan^2\frac{1}{2}\theta$, which is Hill's result. This remarkably simple result for two equal circular apertures may be stated as follows. Let θ be the semi-vertical angle of the cone outside which no radiation incident on one aperture can reach the other. Then the radiation incident on the far face of the circular cylinder formed by the two apertures is reduced by the presence of the cylinder in the ratio $\tan^2\frac{1}{2}\theta : 1$.

No simple method of proof of the final result has suggested itself.

4. The result for a circular cylinder may be compared with Dr. Richardson's result for a cube. Dr. Richardson found that the radiation transmitted in series through two square apertures forming opposite faces of a cube is reduced as compared with what would pass through one aperture alone in the ratio $0{\cdot}6278/\pi = 0{\cdot}1998$.

The corresponding ratio for two circular apertures forming opposite ends of a cylinder of length equal to its diameter, by the above, is $\tan^2\pi/8 = 3 - 2\sqrt{2} = 0{\cdot}1716$. Thus a pair of square apertures separated by a distance equal to their side transmit slightly more radiation than a pair of circular apertures of the same area separated by a distance equal to their diameter.

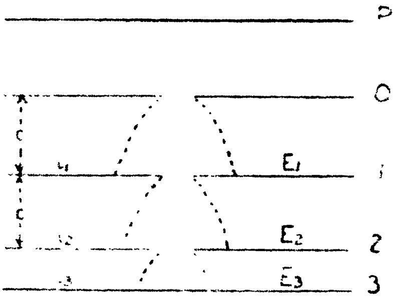
Manchester,
November 20th, 1928.

XXX. *On the Attachment of Electrons to the Molecules HCl and NH_3.* By V. A. Bailey, *M.A., D.Phil.* (*Oxon*), *Associate Professor of Physics, University of Sydney, and* A. J. Higgs, *B.Sc.*[*]

1. A METHOD for the study of the attachment of electrons to gas molecules, and the results of the application of this method to the case of dry air, were described in the issue of this Magazine for October 1925.

The intention there expressed of extending these studies to oxygen has been abandoned, for while the above communication was in the press, the results of an investigation on this gas was published by Dr. H. L. Brose[†], which indicated that very few attachments occur when special precautions are taken to prevent the oxygen from becoming contaminated.

Fig. 1.



It was accordingly decided to investigate the gases hydrogen chloride and ammonia, and to leave for a possible future occasion the more difficult case which suggests itself, that, namely, of chlorine.

2. Before stating the results of these two gases, it is desirable to give a brief outline of the method, the detailed theory of which may be found in the original description[‡].

A uniform electric field of intensity Z is maintained throughout the space between the planes 3 and P in fig. 1 by suitable connexions to a battery of accumulators.

Electrons, emitted by the plate P under the influence of ultra-violet light, move downwards through the gas so that diverging streams of electrons and negative ions pass through the slits in the electrodes E_1, E_2, and E_3, as indicated by the dotted lines.

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[*] Communicated by Prof. J. S. Townsend, F.R.S.

[†] H. L. Brose, Phil. Mag. p. 536 (Sept. 1925).

[‡] V. A. Bailey, Phil. Mag. p. 825 (Oct. 1925).

The number $\alpha n\,.dz$ negative ions are formed by attachment of electrons to molecules when n electrons move a distance dz in the direction of Z. It is easily shown that

$$\alpha = hu/l\mathrm{W}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where h is the probability that an electron of velocity u should attach itself permanently to any molecule it may encounter, W is the mean velocity of drift of the electrons in the direction of Z, and l is the mean free path of an electron between successive collisions with molecules, the gas being at a pressure p. It follows that for a given gas α/p is a function of Z/p alone when Z and p are varied.

The divergence of electrons or ions is expressed by the same curve $y=\mathrm{R}(x)$, where y is the fraction of an approaching stream which passes through a slit, and x represents Z/k for electrons and Z for ions, k being the mean energy of an electron in terms of the mean energy of a molecule at 15° C. This curve, named the Normal Distribution Curve, may be calculated, or determined experimentally, for each diffusion chamber 01 and 12.

The two quantities k and α are separately unknown, but the function of them,

$$a = \mathrm{R}(\mathrm{Z}/k)e^{-\alpha c}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

can be determined experimentally as follows :—

The ratios $\xi=i_2/i_1$ and $\eta=i_3/i_2$ of the currents to the electrodes are measured accurately, and the distribution ratios S_1 and S_2 calculated by means of the formulæ :

$$S_1 = \frac{\xi(1+\eta)}{1+\xi(1+\eta)}, \qquad S_2 = \frac{\eta}{1+\eta}.$$

The ratios R′ and R″ corresponding to the known value of Z for the chambers 01 and 12 respectively are obtained from the Normal Distribution Curves, and then a may be calculated by means of the formula :

$$a = S_1(\mathrm{R}''-S_2)/(\mathrm{R}'-S_1).$$

To obtain another relation between k and α, a_n is similarly determined from observations with the intensity Z/n and the pressure p/n, giving

$$a_n = \mathrm{K}(\mathrm{Z}/kn)e^{-\alpha n/c}.$$

The combination of this with (2) provides a pair of simultaneous equations in two unknown variables, which may then be solved by a graphical operation *.

3. The study of HCl and NH_3 was undertaken with the apparatus used in the examination of air, so an additional detailed account of it is unnecessary.

HCl gas was evaporated *in vacuo* from some of the middle fraction of a twice-distilled aqueous solution of pure HCl, and roughly dried over strong H_2SO_4. Then one part was stored over concentrated H_2SO_4 in a glass reservoir connected with the main apparatus through a mercury-sealed glass tap, and the other was similarly stored over anhydrous P_2O_5, both parts being at about 150 mm. pressure.

After the lapse of five months, samples of each were separately admitted to the mercury gauges and the diffusion instrument up to a pressure of $\frac{1}{2}$ mm., and with $Z=20$ volts/cm. values of S_1 and S_2 were determined, as shown in the following table :—

Desiccator.	S_1.	S_2.
H_2SO_4	·729	·759
P_2O_5	·763	·801

The pair of values in the last line correspond closely to the distribution ratios determined for ions, namely

$$R' = \cdot 754, \qquad R = \cdot 802\,;$$

so from these and other similar determinations it was concluded that the gas stored over H_2SO_4 was drier than that kept over P_2O_5. This was confirmed by the observation that within a few hours the latter formed a skin on the surfaces of mercury in the gauges which adhered to the glass walls in a troublesome manner, whereas the former left the gauges clean, even after many days. Consequently, only the gas dried over H_2SO_4 was investigated.

In the early experiments it was found that adsorption of gas by the internal surfaces of glass and metal reduced the pressure by several per cent. during the course of the observations. This effect was considerably diminished by saturating the surfaces overnight with gas at a pressure in the neighbourhood of those used on the following day. The practice adopted of removing this gas by pumping and washing out with hydrogen before introducing fresh gas, in no way reduced the efficacy of this procedure, as, even in a good vacuum, the surfaces take a long time to give up most of their adsorbed gas.

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* *Loc. cit.* pp. 838–841.

The surface exposed to the ultra-violet light was of copper, and gave an exceptionally good emission in the presence of HCl.

As illustrations some of the individual observations are shown in Table I., but the values of $-\log_{10} a$ given in Table II. are the means of several observations.

The results for values of Z/p less than 10 or greater than 40 are not given, for the first indicated values of k are too low to allow of accurate deductions about a, and the second correspond to the occurrence of ionization by collisions of electrons with molecules which tends to falsify the calculations.

Table I.

HCl.

p.	Z.	k.	η.	S_1.	S_2.	$-\log_{10} a$.	Z/p.
mm.	volts cm.						
1·0	10	·483	1·97	·589	·663	·542	10
·50	5	·378	·960	·426	·490	·524	10
·50	10	·357	2·35	·545	·702	1·18	20
·50	20	·258	3·23	·622	·763	1·06	40
·25	5	·253	1·17	·555	·639	·991	20
·25	10	·193	1·42	·519	·587	·954	40
·125	5	·170	·991	·253	·498	1·00	40

It may be seen from Table I. that, despite the low pressure used, the electrons attach themselves rapidly to molecules, for the ratios S_2 are notably greater than the corresponding ratios S_1, especially with the higher values of Z/p.

The values of k and a determined by the graphical method are shown in Table II., and the former are also represented by a curve in fig. 2 for comparison with the values of k in other gases.

It thus appears that for Z/p greater than 8 the energy of agitation of electrons in HCl is much lower than the energy of electrons in all the common gases examined to date[*], namely H_2, N_2, O_2, CO_2, CO, NO, N_2O, and NH_3.

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[*] J. S. Townsend, 'Motion of Electrons in Gases' (Clarendon Press, Oxford).

If the values of the velocity W were known, it would be possible to determine the values of λ, the fraction of their own energy lost by electrons in collisions with molecules, and of h, the probability of attachment. In the absence of such information, rough estimations may be made by assuming a value of the mean free path L (at 1 mm. pressure) deduced from measurements of the viscosity of HCl, namely $L = 1 \cdot 96 \times 10^{-2}$ cm., and using the formulæ :

Fig. 2.

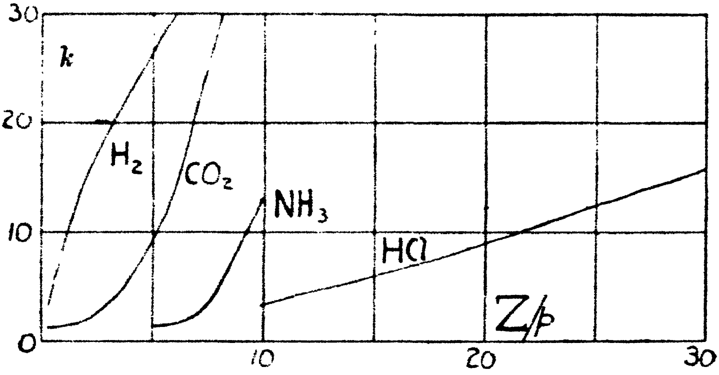

TABLE II.

Z/p.	p.	Z.	$-\log_2 a$.	k.	a.	a/p.
	mm.	volts cm.				
10	1·0	10	·541	3·2	·139	·133
	·50	5	·547		·063	
20	·50	10	1·15	8·9	·375	·750
	·25	5	·992		·187	
40	·50	20	1·06	25	·273	·543
	·25	10	·988		·135	
	·125	5	1·09			

$$\lambda = 305\, L^2 (Z/p)^2 / k^2,$$

$$h = 11 \cdot 1\, (a/p)\, L^2 (Z/p) / k.$$

Thus for $Z/p = 20$ it appears that $\lambda = 59$ per cent. and $h = 7 \times 10^{-13}$.

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* Roth-Scheel, 'Konstanten der Atomphysik.'

4. Some preliminary experiments with NH_3 having shown that the gas reacted vigorously with the available P_2O_5, it was decided to adopt the desiccator recommended by C. Matignon * for the purpose of drying NH_3, namely the grey powder formed by pounding the metallic sodium with fused NaCl. This was considered to be simpler than purifying the P_2O_5 as recommended by Brereton Baker †.

One sample of gas was prepared by evaporation from an aqueous solution, stored first over KOH sticks for several months and finally over Matignon's desiccator. A second sample was prepared by heating *in vacuo* a mixture of pure ammonium chloride and calcium oxide, and passing the gas through a long tube containing KOH and Matignon's mixture into a flask containing the latter alone.

After the lapse of several days these two samples were investigated in the diffusion instrument, and found to give substantially the same results, whose mean values are given in Table III.

As with HCl, it was necessary to reduce the large effects of adsorption by a preliminary saturation of the internal surfaces with the gas.

The values of S_1 and S_2 corresponding to $Z/p=8$ are remarkable in that S_1 is *greater* than S_2 at three pressures out of the five recorded. Another anomaly which shows itself with this value of Z/p is the notable *increase* with the pressure p of the apparent value of k estimated from the values of S_1 (or S_2). The latter anomaly also appears notably for $Z/p=9$.

In the face of these results it was clearly of no advantage to carry out the usual calculations, as these are based on considerations which seem to be violated.

It is probable, however, that the magnitudes of k determined from S_1 as if no ions existed are of some value, and these are accordingly given in the sixth column of Table III. under k_1.

For the values 6, 7, 8, and 9 of Z/p the close agreement between S_1 and S_2 indicates that few ions, if any, are formed by attachment.

For the values of Z/p greater than 9, S_2 is much larger than S_1, which indicates that a considerable amount of attachment is occurring at the higher velocities of the electrons.

The curve for NH_3 in fig. 2 represents the order of the values of k given in the sixth column of Table III., and from this it will be noticed that k is the same low order for NH_3 and HCl when Z/p is less than 7, but for higher values k increases very rapidly with Z/p in NH_3.

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* C. Matignon, *Bull. de la Soc. Chim.* t. 3, no. 58, p. 353 (1908).

† Journal of the Chem. Soc. lxxiii. p. 422 (1898).

Table III.

NH_2.

Z/p.	p.	Z.	S_1.	S_2.	k_1.	k_2.
5	4	20	·777	·801	1·19	
	2	10	·670	·699	1·31	
	1	5	·533	·575	1·38	
6	4	24	·779	·795	1·40	
	2	12	·667	·686	1·61	
	1	6	·541	·572	1·58	
	·5	3	·416	·442	1·53	
7	2	14	·614	·611	2·55	
	1	7	·519	·525	2·08	
	·5	3·5	·392	·407	2·02	
8	8	64	·745	·701	5·0	7·4
	4	32	·589	·594	6·60	6·83
	2	16	·520	·499	4·71	5·6
	1	8	·416	·409	4·08	4·6
	·5	4	·328	·331	3·75	3·2
9	2	18	·415	·439	9·23	8·78
	1	9	·312	·331	8·17	8·34
	·5	4·5	·262	·269	5·84	6·08
10	2	20	·377	·509	12·65	
	1	10	·268	·379	12·20	
	·5	5	·207	·270	9·43	
15	1	15	·376	·727	9·5	
	·5	7·5	·249	·552	12·3	
20	1	20	·512	·779	6·1	
	·5	10	·332	·645	8·9	

If some such rapid variation be the cause of the anomalies which appear with $Z/p=8$, then to account through an instrumental error for the observations a much more rapid variation of k with Z/p must exist than is indicated by the above curve (fig. 2).

In the middle of the series of observations with NH_3 the instrument was thoroughly freed of this gas by means of a side-tube containing H_2SO_4 and re-tested with H_2 gas at pressures of 10 mm. and 32 mm. The measured values of S_1 and S_2 were in complete agreement with the standard distribution curves, for which S_1 is always about 40 per cent. less than S_2; so instrumental variations cannot be invoked in explanation.

A full discussion of the possible cause of the anomalies is better postponed to some future occasion, when the gas can be examined under more flexible conditions, to provide which a new instrument has been constructed.

For the present we may consider that the cause is possibly given by one of the following :—

(1) The electrons emitted by the plate issue with an energy of about 2 volts, and so may form some ions which subsequently change to electrons and neutral molecules.

(2) As indicated below, the gas contained a small quantity of H_2, and a small change in the concentration of this might well produce large effects, since k appears to vary rapidly with Z/p. Such a change in concentration would occur by the process of *effusion* through the tap admitting gas to the instrument.

Nearly a year after the above investigations were made, Mr. J. D. McGee examined with the new instrument the NH_3 gas left over by us, and obtained totally different results which more really resemble those for H_2. The containing flask was then opened with a flame, and the resulting small explosion and flash confirmed the supposition that the flask which formerly contained NH_3 now contained a considerable quantity of H_2.

There is no doubt that this is due to the slow decomposition of NH_3 by the sodium desiccator with formation of sodamide and hydrogen, and so it may be concluded that Matignon's method of drying is not fully satisfactory with this gas.

In the original experiments, repetitions of the observations after intervals of about a week had not shown any serious discrepancies, so the results given are probably of the right order for NH_3.

5. Nothing in these experiments supports the view that k is independent of the velocity of the electrons ; the contrary[*] is made to appear probable, especially in the case of NH_3.

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[*] V. A. Bailey, Phil. Mag. xlvi. p. 218 (July 1923).

From these and earlier observations it may be provisionally concluded that with air, NO[*], and H_2O [*] h diminishes as the velocity increases, and that h increases with the velocity in N_2O [†], NH_3, and HCl over the range studied.

It is interesting to note that the gases H_2O, NH_3, and HCl, which appear to have relatively large values of h, also have relatively large values [‡] of K−1. So it may be of value to examine a possible association between h and the electric moment μ of a molecule. This quantity μ can be calculated from the variation of the dielectric constant K with temperature, by a theory due to Debye [§], and its approximate values for a number of different molecules are given in the following table:—

Molecule.	H_2, N_2, O_2, C_2H_4, rare gases.	CO.	CO_2.	H_2O.	NH_3.	HCl.	Cl_2.
$\mu \times 10^{18}$.	Negligible.	1·2	1	1·8	1·5	1·5	1·3

For the molecules H_2, N_2, O_2, He, A, CO, CO_2, C_2H_4, which have low values of μ, h is known to be negligible, while for the molecules H_2O, NH_3, and HCl both μ and h are large.

The case of Cl_2 is of special interest, as its low value of μ suggests that this *molecule* has no great affinity for electrons, contrary to the conclusions of L. B. Loeb [||] that h is greater than 5×10^{-4}. In view of the large affinity of HCl for electrons and the difficulty of preparing and keeping Cl_2 gas free from HCl through its great chemical activity, and the presence of sources of H_2 in the usual measuring apparatus, this is not surprising.

An analogous case is that of O_2, which was thought to have a considerable affinity for electrons, until the experiments of H. L. Brose [¶] showed that very few electronic attachments occur in the gas.

It is therefore highly desirable that experiments be conducted on very pure Cl_2 to examine this point.

[*] Skinker & White, Phil. Mag. xlvi. (October 1923).

[†] J. S. Townsend, 'Electricity in Gases,' p. 287. (Clarendon Press.)

[‡] Schrödinger, 'Graetz Handbuch der Electrizität . . .' i. p. 192.

[§] Victor Henri, 'Structure des Molecules,' pp. 16–26 (J. Herman, Paris). K. T. Compton, 'Science,' Jan. 15, 1926. O. Blüh, *Phys. Zeits.* xxvii. p. 226 (1926).

[||] L. B. Loeb, 'Kinetic Theory of Gases' (McGraw Hill).

[¶] *Loc. cit.*

In conclusion we may notice that the experiments described here appear also to indicate that the adsorptive properties of a molecule are related to its *h*, which is in agreement with the known general correspondence between molecular polarity and adsorption.

Summary.

The method for the study of the attachment of electrons to molecules described in 1925 is applied to HCl and NH_3, and the results serve to indicate a certain correspondence between the probability of attachment to a given molecule and its electric moment as deduced from variations of dielectric constant with temperature.

XXXI. *On the Ionization Potentials of the Rare Earth Elements in relation to their position in the Periodic System.*

By L. Rolla *and* G. Piccardi, *Instituto di Chimica generale della R. Università, Firenze (Italia)*[*].

THE binding forces with which the valency electrons are retained in an atom can best be measured by determining the ionizing potentials. In the case of the rare earths the spectroscopic data are insufficient to place the lines in series and so calculate the corresponding terms. Indirect means have been used in order to arrive at a classification of the elements between barium and hafnium. Thus measurements of atomic and molecular volumes of the elements and similar compounds have been used to give interesting figures. In this case the greater the binding strength the greater will be the contraction in isomorphous compounds.

Goldschmidt, Ulrich, and Barth$^{(1)}$ have determined the molecular volumes of the sesquioxides of the rare earths by the X-ray spectrographic method, and established the law that the molecular volume, in the crystalline compounds examined, diminishes with increasing atomic number. The work of V. Hevesy$^{(2)}$ on the series of the octo-hydro-sulphates and of Jantsch$^{(3)}$ on the double nitrates of magnesium confirm these results. The atomic volumes of the six elements (La, Ce, Pr, Nd, Sa, Yb) have also been measured, and, in spite of the large experimental errors, it seems as if one

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[*] Communicated by the Authors.

ought to regard the contraction with increasing atomic number as demonstrated, in agreement with theory.

Astrophysical observations give to the rare earths a place of special importance in the constitution of the stars, and lead to conclusions of great value in the present problem.

In the solar spectrum (absorption spectrum) Rowland (4) recognized and catalogued in his tables 36 lines belonging to Ce, 17 to Nd, 32 to Y, 20 to Sc, and 69 to La.

Successive studies revealed an ever-increasing number of lines, and the elements Er, Eu, Gd, Pr, Sm, Dy were also recognized in the solar spectrum.

During the total eclipses of the Sun it is possible to photograph the spectrum of a very thin crescent of the solar chromosphere. In this case the crescent itself is used as the slit of the spectroscope, and is made up of many arcs of circles whose width varies with the height of the solar chromosphere from which the various elements radiate. Mitchell (5) and St. John (6), who studied this spectrum, came to the conclusion that all the rare earths present in the sun occur in the lower layer of the chromosphere from 0 to 500 km. high. Only La and Y reach a height of 600 km. From our knowledge of ionizing potentials we can account for these facts, and consequently a study of ionizing potentials is of great value in the interpretation of stellar spectra.

The validity of the mass-action law has been demonstrated for the case of atomic ionization into an electron and a positive ion. We can write, therefore,

$$\text{Neutral atom} \rightleftharpoons \text{positive ion} + \text{electron.} \quad . \quad . \quad (1)$$

By use of this equation notable progress has been made in astrophysics, especially by Megh Nad Saha (7). It follows that the equilibrium constant K of equation (1), *i.e.* $[A^+]$, [electron], [neutral atom] is connected with the heat of reaction, *i. e.* the ionizing energy (U), and with the absolute temperature (T) by the equation expressing the law of mobile equilibrium:

$$U = -RT^2 . \frac{d \log K}{dT} . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In astrophysics the experimental determination of K is made by measuring the relation between the intensity of the arc lines (neutral atom) and of the spark lines (ionized atom) for the same element. Knowing U, we can calculate T, or, conversely, if T is known we can calculate U.

The distribution of the rare-earth elements in the solar chromosphere shows that their ionizing potentials vary very little with increasing atomic number. In work of a physico-chemical nature it is necessary to establish the validity of equation (1), and so arrive at a value of U by using (2).

We have solved this problem in a satisfactory manner with an experimental method of great simplicity (8).

A flame, which may be regarded as a stationary phenomenon, goes through a fine metallic gauze and hits a metal plate which is connected electrically to the gauze. By creating a difference of temperature between the gauze and the plate, a current flows continuously. No difference of potential is applied from outside. If, now, we introduce atoms (A) capable of being ionized under the said conditions into ions (A′) and electrons, the ions will discharge on one electrode and the electrons on the other (gauze or plate).

The difference in the current measured in the flame with and without atoms (A) gives us a measure of the number of electrons and ions which pass in one second between the electrodes.

Thus, when we know the number of neutral atoms passing per second from one electrode to the other, we have all the necessary data for calculating the rate of dissociation of (A) and the equilibrium constant of (1).

The current measured in this way is the result of movement of both positive and negative charges.

If the flame produced only positive or only negative charges, no current would flow. Thus, when an incandescent source of electrons such as platinum or iridium wire, bare or covered with a layer of non-volatile oxide, is placed below the gauze, we do not observe any variations of current.

This can be understood from the special form of cell that we used.

The final current can only be due to the simultaneous discharge of positive and negative charges in equal quantity.

In the first experiment we worked with an ordinary Bunsen flame. Into its upper part, which is homogeneous, we introduced two flat electrodes—the lower made of a net of platinum wire 0·1 mm. thick, with a 4-mm. mesh, the upper made also of platinum 15 × 20 mm. and 0·1 mm. thick.

The distance between net and plate was not less than 6 mm. nor more than 8 mm. A mirror galvanometer 160 ohms internal resistance and giving a deflexion of 1 cm. $= 2{\cdot}475 \times 10^{-7}$ amp. at 2 metres was inserted between the net and the plate. The galvanometer in this case acts as an ammeter, since its resistance is negligible compared with the resistances of the flame between the electrodes. An experiment is carried out in the following manner:—After fixing the electrodes at a certain distance, we measure the current in the ordinary Bunsen flame (this gives a current of the order of 10^{-8} amp.). If the inrush of gas and of air are well regulated, the current is absolutely constant. At a given instant we introduce under the net a bead containing a known quantity of salt, and measure the current and its variation with time. Then the bead is withdrawn, and it is observed that the current falls to its initial value.

Table I.

Element.	Salt.	Atoms/sec.	Dissociation.	K.
Sodium.	Na_2SiO_3	$3{\cdot}44 . 10^{15}$	$1{\cdot}41 . 10^{-1}$	$6{\cdot}35 . 10^{9}$
	$Na_2B_4O_7$	$4{\cdot}50 . 10^{16}$	$3{\cdot}95 . 10^{-2}$	$6{\cdot}40 . 10^{9}$
	,,	$8{\cdot}66 . 10^{16}$	$2{\cdot}66 . 10^{-2}$	$6{\cdot}10 . 10^{9}$
	Na_2CO_3	$4{\cdot}03 . 10^{17}$	$3{\cdot}80 . 10^{-3}$	$6{\cdot}03 . 10^{9}$
	,,	$5{\cdot}14 . 10^{17}$	$3{\cdot}33 . 10^{-3}$	$5{\cdot}75 . 10^{9}$
	Na_2SiO_3	$1{\cdot}23 . 10^{15}$	$1{\cdot}25 . 10^{-1}$	$1{\cdot}90 . 10^{9}$
	$Na_4P_2O_7$	$1{\cdot}80 . 10^{16}$	$1{\cdot}12 . 10^{-2}$	$2{\cdot}20 . 10^{9}$
	Na_2CO_3	$2{\cdot}69 . 10^{17}$	$7{\cdot}35 . 10^{-3}$	$1{\cdot}44 . 10^{9}$
	,,	$4{\cdot}07 . 10^{17}$	$6{\cdot}40 . 10^{-3}$	$1{\cdot}68 . 10^{9}$
	NaCl	$4{\cdot}36 . 10^{15}$	$1{\cdot}85 . 10^{-3}$	$1{\cdot}59 . 10^{9}$
	$Na_2B_4O_7$	$4{\cdot}18 . 10^{16}$	$4{\cdot}85 . 10^{-2}$	$9{\cdot}85 . 10^{9}$
	,,	$1{\cdot}34 . 10^{17}$	$2{\cdot}67 . 10^{-2}$	$9{\cdot}67 . 10^{9}$
Barium.	$BaCl_2$	$2{\cdot}02 . 10^{16}$	$1{\cdot}00 . 10^{-1}$	$2{\cdot}00 . 10^{10}$
	,,	$4{\cdot}62 . 10^{16}$	$6{\cdot}60 . 10^{-2}$	$2{\cdot}00 . 10^{10}$
	$BaCl_2$	$8{\cdot}93 . 10^{15}$	$1{\cdot}97 . 10^{-1}$	$3{\cdot}40 . 10^{10}$
	,,	$1{\cdot}20 . 10^{16}$	$1{\cdot}55 . 10^{-1}$	$2{\cdot}88 . 10^{10}$
	,,	$3{\cdot}21 . 10^{16}$	$1{\cdot}01 . 10^{-1}$	$3{\cdot}30 . 10^{10}$
	$BaCl_2$	$3{\cdot}46 . 10^{16}$	$5{\cdot}67 . 10^{-2}$	$1{\cdot}10 . 10^{10}$
	,,	$5{\cdot}75 . 10^{16}$	$4{\cdot}71 . 10^{-2}$	$1{\cdot}10 . 10^{10}$
Lithium.	Li_2SO_4	$1{\cdot}55 . 10^{16}$	$4{\cdot}02 . 10^{-3}$	$2{\cdot}52 . 10^{7}$
	,,	$2{\cdot}33 . 10^{16}$	$3{\cdot}55 . 10^{-3}$	$2{\cdot}93 . 10^{7}$
	,,	$5{\cdot}53 . 10^{16}$	$2{\cdot}10 . 10^{-3}$	$2{\cdot}47 . 10^{7}$
	Li_2SO_4	$1{\cdot}85 . 10^{16}$	$8{\cdot}48 . 10^{-3}$	$1{\cdot}31 . 10^{8}$
	,,	$2{\cdot}56 . 10^{16}$	$7{\cdot}80 . 10^{-3}$	$1{\cdot}57 . 10^{8}$
	,,	$1{\cdot}21 . 10^{17}$	$3{\cdot}27 . 10^{-3}$	$1{\cdot}34 . 10^{8}$
	Li_2SO_4	$6{\cdot}99 . 10^{15}$	$8{\cdot}38 . 10^{-3}$	$4{\cdot}91 . 10^{7}$
	,,	$1{\cdot}34 . 10^{17}$	$1{\cdot}86 . 10^{-3}$	$4{\cdot}66 . 10^{7}$

Having plotted the values of current intensity against time, we take the mean ordinate and subtract from it the value of the current produced in the pure flame. We then know the mean value of the ionization current, and from this follows immediately the concentration of the ions $[A^+]$ and of the electrons $[e]$, since we know the charge on an electron, and the two concentrations in (1) must be equal.

We also know, from the loss of weight of the bead and the duration of the experiment, the number of atoms introduced per second into the flame. Under the conditions of the Bunsen flame this number is practically the same as the number of neutral atoms.

We now have all the data necessary to calculate the equilibrium constant of (1).

By proper choice of the metallic salt we can obtain uniform evaporation, as shown by the constancy of the current during any experiment.

Thus for the first time we have been able to demonstrate experimentally the law of mass action for electronic equilibrium. The measurements always give the same value of K for the same atom and experimental conditions, though working at different concentrations.

Calculation of the Ionizing Potential.

We can, then, on a thermodynamic basis, apply equation (2) to obtain U the ionizing energy. The calculation is simplified if we regard U as independent of the temperature, so that if K_1 and K_2 are the equilibrium constants of (1) for temperatures T_1 and T_2, we have

$$\log K_2 - \log K_1 = \frac{U}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

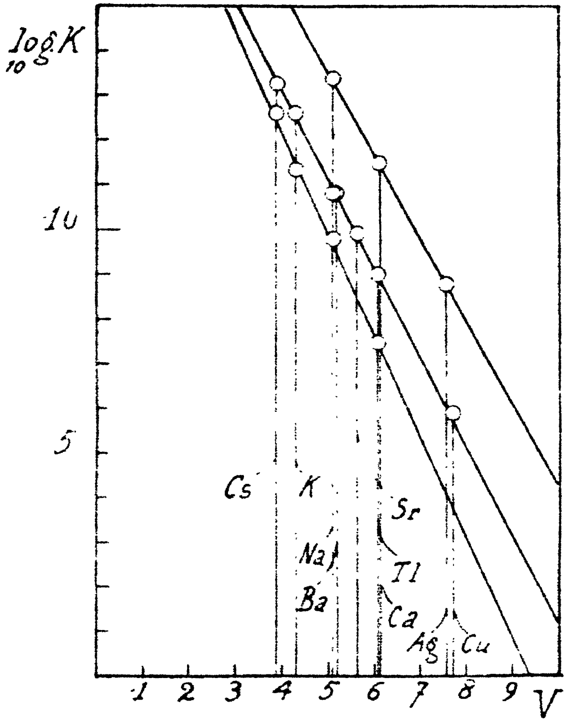
We have found that in the case of sodium the formula leads to results agreeing with those obtained spectroscopically.

We can simplify still further by integrating (2):

$$\log K = -\frac{U}{RT} + C, \qquad \ldots \ldots \quad (3)$$

where C is a constant of integration. Then, if we take two elements whose ionization potential is known, we can determine the constants of (3) for a standard flame. We can then determine U for every element by measuring log K under the given conditions. Our experiments have shown that the relation between V (ionizing potential) and log K is linear (see fig. 1 and Table II.)*. The three straight lines were obtained by varying the rate of flow and temperature of the flame.

Fig. 1.



The slope of the line is

$$-\frac{1}{RT} = \tan \alpha,$$

and, expressing in volts,

$$\tan \alpha = -\frac{96500 \text{ coulombs}}{4{\cdot}186 \text{ joules} \times RT} = -\frac{23052}{RT},$$

or, in decimal logarithms,

$$\tan \alpha = -\frac{23052}{4{\cdot}571\,T}.$$

---

* This experimental fact agrees with the theory developed by Saha on the basis of Nernst's principle for ionization of the first kind: *the integration constant is the same for all atomic species* (chemical constant).

Table II.

Element.	V.	Log K.	Element.	V.	Log K.	Element.	V.	Log K.
Ca ...	3·89	12·628	Cs ...	3·89	13·270	Na ...	5·11	13·403
K ...	4·32	11·350	K ...	4·32	12·624	Ca ...	6·09	11·498
Na ...	5·13	9·793	Na ...	5·13	10·807	Ag ...	7·64	8·772
Tl ...	6·04	7·487	Ba ...	5·19	10·817			
			Sr ...	5·67	9·923			
			Tl ...	6·04	8·982			
			(Cu ...	7·69	5·905)			

The Influence of the Acid Radicles.

In the above method we have introduced a volatile salt into the flame in order to study equation (1) for the metal atoms. Generally we find that the volatile salts behave as if only the metallic atom would be present. The acid molecules and atoms resulting from the decomposition of the acid radicles have no influence on the ionization phenomenon, in spite of their known electron affinity.

This fact has already been observed by Arrhenius(9), Wilson, and others in some classic researches on the conductivities of salted flames. They showed that in the Bunsen flame the conductivity is independent of the acid radicle.

In our own experiment it is possible to vary the temperature conditions of the flame so that the influence of the anion of the volatilized salt becomes not only sensible but entirely preponderant.

Since the ionization potentials of the atoms I, Cl, S, O, etc., and of the molecules CO_2, SO_2, MoO_3, etc., are in general over 10 volts, we can understand how negligible will be the ionization of the acid radicle and its decomposition products at the temperature of the Bunsen flame.

Similarly, the electron affinity of these atoms and molecules is so small that the diminution in current between the net and plate can also be neglected in comparison with the increase produced by ionization of the metal atoms.

Frequently, however, this diminution is observable, and varies in magnitude with the nature of the anion. Thus, in the equilibrium :

$$\text{Neutral atoms} + \text{electron} \rightleftharpoons \text{negative ions}$$

the direction of the current will be reversed relatively to the current in the case of ionization :

$$A \rightleftharpoons \overset{+}{A} + \ominus.$$

So with flames of proper temperature we ought to observe a reverse current, due to

$$A \rightleftharpoons \overset{-}{A} - \ominus \quad \text{or} \quad A \rightleftharpoons \overset{-}{A} + \oplus.$$

Experiment confirms this (10).

We must make sure, however, that we are observing a reversed current and not simply a diminution, as it might seem at first sight. In the experiments on the conductivity of the salted flame, the electron affinity of an atom or a molecule manifests itself by diminishing the conductivity, *i. e.*, as a simple capture of negative charges ; in our case the phenomenon leads to an inversion of the current.

The method that we have described is applicable to the measurement of electron affinity, as one of us (11) has shown for Br, I, SO_2, SeO_2, and MoO_3.

Ionizing Potentials of the Rare Earth Elements.

The agreement of our results with those where comparison with spectroscopic results was available persuaded us to apply our method to the elements of the rare earths.

We replaced the Bunsen flame by a flame obtained by mixing coal-gas and oxygen so as to realize the temperatures necessary for volatilizing such refractory oxides. We were able to obtain steady gas-flows, so that the conditions may be considered constant.

An iridium net (wires of 0·6 mm. diameter) was used in place of the platinum one, and a thick piece of platinum with folded edges and supported on heavy brass rings formed the upper electrode. In this way there was considerable cooling by conduction, and whilst the iridium net got white-hot the platinum became light yellow.

The slope of the ionization curve was determined relative to sodium and calcium, using the data given in Table III.:—

TABLE III.

Atom.	Log K.	V.
Na	13·403	5·13
Ca	11·498	6·09

and therefore we have

$$\tan\alpha = \frac{13{\cdot}403 - 11{\cdot}498}{5{\cdot}13 - 6{\cdot}09} = -1{\cdot}98.$$

This value is in perfect agreement with that calculated from the temperature of the flame (about 2300° C.). Therefore, when in the formula

$$\tan\alpha = -\frac{23052}{4{\cdot}571\,T}$$

we put $T = 2300° + 273°$, we have

$$\tan\alpha = -1{\cdot}96,$$

and for $T = 2250° + 273°$,

$$\tan\alpha = -2{\cdot}00.$$

In order to volatilize such refractory oxides as those of the rare earths, we could, for example, use temperatures higher than those obtained in flames; but this is not always possible, as one sometimes melts the iridium net before the oxide is melted.

By exercising great care it has been possible to obtain results for nine oxides :—

Table IV.

Element.	Oxide.	Loss in weight, per sec.	Increase of current *.	Atoms, per sec.	Electr., per sec.	Log K.	V.
La ...	La_2O_3	$2{\cdot}06 . 10^{-6}$	$\overset{\circ}{123}{\cdot}68$	$8{\cdot}10 . 10^{15}$	$1{\cdot}93 . 10^{14}$	12·662	5·49
Ce ...	CeO_2	$5{\cdot}53 . 10^{-6}$	7·61	$1{\cdot}92 . 10^{16}$	$1{\cdot}18 . 10^{13}$	9·866	6·91
Pr ...	Pr_4O_7	$2{\cdot}34 . 10^{-6}$	72·25	$8{\cdot}38 . 10^{15}$	$1{\cdot}12 . 10^{14}$	12·168	5·76
Nd ...	Nd_2O_3	$1{\cdot}26 . 10^{-6}$	15·88	$4{\cdot}50 . 10^{15}$	$2{\cdot}48 \cdot 10^{13}$	11·133	6·31
Sa ...	Sa_2O_3	$1{\cdot}23 . 10^{-6}$	8·07	$4{\cdot}23 . 10^{15}$	$1{\cdot}26 . 10^{13}$	10·576	6·55
Gd ...	Gd_2O_3	$1{\cdot}24 \cdot 10^{-6}$	6·16	$4{\cdot}12 . 10^{15}$	$9{\cdot}61 . 10^{12}$	10·406	6·65
Tb ...	Tb_4O_7	$2{\cdot}66 . 10^{-7}$	2·40	$8{\cdot}53 . 10^{14}$	$3{\cdot}75 . 10^{12}$	10·212	6·74
Dy ...	Dy_2O_3	$1{\cdot}48 . 10^{-7}$	1·50	$4{\cdot}76 . 10^{14}$	$2{\cdot}34 . 10^{12}$	10·060	6·82
Yb ...	Yb_2O_3	$1{\cdot}04 . 10^{-6}$	2·16	$2{\cdot}79 . 10^{15}$	$5{\cdot}35 . 10^{12}$	9·582	7·06

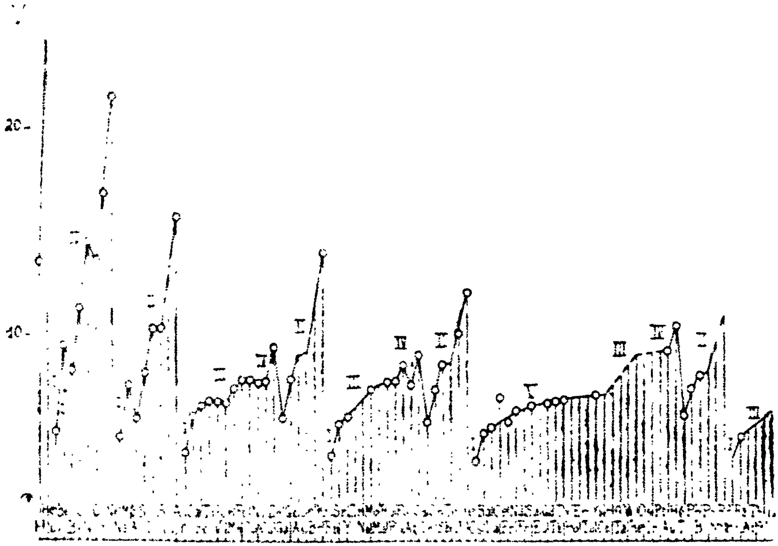
* $1° = 2{\cdot}475 . 10^{-7}$ amp.

The values in the fifth column have been obtained on the assumption that the oxide is dissociated into oxygen and metal, and that the metal is, at these temperatures, monatomic. This is legitimate owing to the extreme dilution.

Ionizing Potentials and the Periodic System.

If we plot the known ionization potentials obtained both spectroscopically and by the method described above against the atomic numbers of the elements, we obtain a curve showing the periodicity of Mendelejeff's system, which is in perfect agreement with the theory of atomic constitution (fig. 2). Here we notice the large abrupt falls of ionizing potential separating the short periods H–He, Li–Ne, Na–Ar; the two long periods of 18 elements each, K–Kr and Rb–Xe; and finally the longest period of 32 elements, Cs–Rd and in part of the period 87–U.

Fig. 2.



The curve presents some characteristic marks which repeat themselves in the various periods. These marks are found to occur in the different periods at elements which bear a chemical resemblance to one another.

The marks I and II appear in all the periods; the mark III in the three long periods and in the portion of the period which completes the system; the mark IV in the long periods; whilst the mark V, which covers all the rare earth elements, occurs only in the longest period of 32 elements.

Hydrogen finds no homologous element in the system, and we can only relate it vaguely with the alkali metals; this fact is in perfect harmony with the peculiar nature of this element; nor can we find homologues for the rare earths, and this agrees with the peculiarity of mark V. This preliminary examination shows clearly that the magnitudes of the ionizing potentials lend themselves beautifully to the representation of the periodic properties of the elements and to the grouping into periods and subperiods. This property is certainly due to the fact that the ionizing potential is characteristic of the free atom unaffected by valency or crystal bindings. The ionizing potential is measured when the elements are in the state of monatomic gases.

TABLE V.—Table of Ionization Potentials.

No.	Element.	V.	No.	Element.	V.	No.	Element.	V.
1 ...	H	13·53	32 ...	Ge	7·8	63 ...	Eu	—
2 ...	He	24·41	33 ...	As	—	64 ...	Gd	6·65
3 ...	Li	5·37	34 ...	Se	—	65 ...	Tb	6·74
4 ...	Be	9·5	35 ...	Br	—	66 ...	Dy	6·82
5 ...	B	8·34	36 ...	Kr	13·9	67 ...	He	—
6 ...	C	11·3	37 ...	Rb	4·16	68 ...	Er	—
7 ...	N	14·49	38 ...	Sr	5·67	69 ...	Tu	—
8 ...	O	13·56	39 ...	Y	6	70 ...	Yb	7·06
9 ...	F	16·9	40 ...	Zr	—	71 ..	Cp	—
10 ...	Ne	21·47	41 ...	Nb	—	72 ...	Hf	—
11 ...	Na	5·11	42 ...	Mo	7·35	73 ..	Ta	—
12 ...	Mg	7·61	43 ...	Ma	—	74 ..	W	—
13 ...	Al	5·96	44 ...	Ru	7·7	75 ...	Re	—
14 ...	Si	8·19	45 ...	Rh	7·7	76 ...	Os	—
15 ...	P	10·3	46 ...	Pd	8·5	77 ...	Ir	—
16 ...	S	10·31	47 ...	Ag	7·54	78 ...	Pt	—
17 ...	Cl	—	48 ..	Cd	8·95	79 ...	Au	9·25
18 ...	A	15·69	49 ...	In	5·76	80 ...	Hg	10·39
19 ...	K	4·32	50 ..	Sn	7·35	81 ...	Tl	6·08
20 ...	Ca	6·09	51 ...	Sb	8·5	82 ...	Pb	7·39
21 ...	Sc	6·57	52 ...	Te	—	83 ...	Bi	8
22 ...	Ti	6·81	53 ...	I	10	84 ...	Po	—
23 ...	V	6·76	54 ...	Xe	12	85 ...	—	—
24 ...	Cr	6·67	55 ...	Cs	3·89	86 ...	Rd	—
25 ...	Mn	7·41	56 ...	Ba	5·19	87 ...	—	—
26 ...	Fe	7·83	57 ...	La	5·49	88 ...	Ra	5 ?
27 ..	Co	7·81	58 ...	Ce	6·91	89 ...	Ac	—
28 ...	Ni	7·64	59 ...	Pr	5·76	90 ...	Th	—
29 ...	Cu	7·69	60 ...	Nd	6·31	91 ...	—	...
30 ...	Zn	9·35	61 ...	Fr	—	92 ...	U	—
31 ...	Ga	5·97	62 ...	Sa	6·55			

For H, He, Ne, A, Kr, Xe, O, S, Li, Na, K, Rb, Cs, Cu, Ag, Au, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg, B, Al, Ga, In, Tl, Cr, Mn, Mo, Bi, Pb, Sb, I, see (13); for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, see (14), (15), and (16); for Ru, Rh, Pd, see (17); for Be, B, C, N, F, Ne, see (18); for A, see (13) and (19); for Kr and Xe, see (13) and (20); for Sn, see (21); for B, see (18) and (22); for F, see (18) and (23); for P, see (24).

TABLE VI.—Periods.

Marks.	I.	II.	III.	IV.	V.	VI.
I.	Li	Na	K	Rb	Ce	87
	Be	Mg	Ca	Sr	Ba	Ra
II.	B	Al	Ga	In	Tl	—
	C	Si	Ge	Sn	Pb	—
	N	P	As	Sb	Bi	—
	O	S	Se	Te	Po	—
	F	Cl	Br	I	85	—
	Ne	Ar	Kr	Xe	Rd	—
III.	—	—	Sc	Y	La	Ac
	—	—	Ti	Zr	Hf	Th
	—	—	V	Nb	Ta	91
	—	—	Cr	Mo	W	U
	—	—	Mn	Ma	Re	—
	—	—	Fe	Ru	Os	—
	—	—	Co	Rh	Ir	—
	—	—	Ni	Pd	Pt	—
IV.	—	—	Cu	Ag	Au	—
	—	—	Zn	Cd	Hg	—
V.	—	—	—	—	Ce	—
	—	—	—	—	Pr	—
	—	—	—	—	Nd	—
	—	—	—	—	Fr	—
	—	—	—	—	Sa	—
	—	—	—	—	Eu	—
	—	—	—	—	Gd	—
	—	—	—	—	Tb	—
	—	—	—	—	Dy	—
	—	—	—	—	Ho	—
	—	—	—	—	Er	—
	—	—	—	—	Tu	—
	—	—	—	—	Yb	—
		—	—	—	Cp	—

The curve presents some striking characteristics which are in agreement with our ideas of atomic structure, based upon the theories of Bohr and Hund(25) :—

(1) The addition of an electron in any orbit produces in general an increase * in the ionizing potential ; this increase is greater for additions to external than to internal orbits. The steepest portions of the diagram are the parts H–He, I, II, and IV, in which the added electron goes into an

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* Except in the passage from nitrogen to oxygen, from phosphorus to sulphur etc., *i. e.*, from a 5-valent to a 6-valent element. This fact, which finds agreement with other facts, cannot as yet be explained precisely.

outer orbit (*s* or *p*) ; much less inclined are the portions III of the long periods, in which the added electron enters the orbit immediately within the outermost (orbit *d*). The portion V containing the rare earths is still less inclined. Here the electron enters orbits still nearer the nucleus (orbit 4*f*, where the external orbit is 6*s*).

Expressing these variations of the ionizing potentials by mean numbers, which must only be taken as illustrative, we observe that:

(*a*) For the addition of an electron to an *s* orbit the potential receives an increment included between 1·2 and 11 volts, while for the orbit *p* the increment is included between 0·82 and 2·25 volts.

(*b*) For the addition to a *d* orbit the potential increases by about 0·3 volt.

(*c*) For an addition to an *f* orbit, the case of the rare earths, the potential increases 0·14 volt.

This shows clearly that the potential responds much less for structural changes near the core than for changes in the outer orbits.

(2) When all the possible external orbits of a series are filled, the ionizing potential reaches a maximum. These maxima are represented by the rare gases. (One year after the publication (26) of our curve and its related properties, this fact was independently observed by Megh Nad Saha, who reported in his work (27) a curve of potentials constructed by R. N. Gosh and limited to the first three periods.)

(3) When the *d* orbits, internal to the *s* orbits, become saturated, the ionizing potential again reaches a maximum : these maxima are represented by the divalent metals Zn, Cd, Hg.

(4) The diagram shows two well-defined series of minima, both corresponding to the beginning of a new electronic ring. One series is represented by the alkali metals, and corresponds to the beginning of the *s* orbits ; the other is represented by the trivalent metals B, Al, Ga, In, Tl, and corresponds to the beginning of the second ring of electronic orbits (*p* orbits).

(5) The influence of a change in atomic number over the ionizing potential is different for homologous elements belonging to marks I and II and those belonging to marks III and IV (mark V lies outside these considerations).

For the marks I and II an increase in the atomic number causes a decrease in the ionizing potential ; this diminution is more rapid for elements with high ionizing potentials than for those with low potentials. For example, we observe—

For the inert gases :

He.	Ne.	Ar.	Kr.	Xe.	Rd.
24·49	21·48	15·69	13·3	12·0	?

For the alkaline earth metals :

Be.	Mg.	Ca.	Sr.	Ba.	Ra.
9·50	7·61	6·09	5·67	5·19	5 ?

For the alkali metals :

Li.	Na.	K.	Rb.	Cs.	87.
5·37	5·11	4·32	4·16	3·89	?

In contrast to this we find in marks III and IV that the potentials fall slightly in passing from the third to fourth period, and then rise sharply in passing to the fifth. The rise is clearly due to the insertion of the rare earths, which pushes all the following elements as far as mercury to higher potentials. With the elements below mercury the addition of electrons takes place in internal orbits ; those coming after mercury add electrons to their outer ring (thallium and following), and the ionizing potential behaves normally. This return to normal behaviour after such a perturbation is worth noticing as further evidence of the extent to which the ionization potential depends on the external structure, and of the importance, in theories of atomic constitution, of the very strange group of elements known as the rare earths.

The results found in the above experiments are in perfect agreement with the views of Bohr on general atomic structure and of Hund on the structure of particular elements. It is very interesting to study the marks III, as they should not show similarities too exact, because the triads Fe, Co, Ni ; Ru, Rh, Pd ; Os, Ir, Pt do not contain homologous elements ; in fact, the first two triads are notably different from one another.

(6) We can see also how the ionizing potentials can be taken—though not in an absolute sense—as an index of basicity agreeing with the chemical properties. Thus the elements with a distinct electropositive character—alkali metals, alkaline earth metals, and rare earth metals—have all rather small potentials ; while the elements with a distinct electronegative character—halogens and the nitrogen and oxygen groups—all have high potentials.

The inert gases, whose chemical stability is almost complete, possess in each period the maximum potential.

In the group of noble metals we find still further support for these general views. Thus the most electropositive is undoubtedly silver and the most electronegative is gold (it behaves, from the chemical point of view, as a real metalloid), whilst silver has the lowest ionizing potential, 7·54 volts, and gold the greatest, 9·25 volts.

We will not go further into the detailed examination of the peculiarities of the curve. At present it is enough to have constructed for the first time a sufficiently complete curve of potentials, to have shown how beautifully this represents the periodic system of the elements, and to have shown how to insert the rare earth group.

These values for the rare earths appear on a slightly-curved segment characterized by a small inclination and low values of the ionizing potential; cerium alone is exceptional, and this may be due partly to the fact that the oxide is only slightly dissociated, and partly to the less basic character of this element.

In general we observe that the ionizing potential increases regularly in an almost asymptotic curve with increasing atomic number. This regularity is found in other physical values, *e. g.* the atomic volumes and molecular volumes of similar compounds. No peculiarity appears for elements such as gadolinium, which are believed to possess particular properties; this shows that if these peculiarities exist, their origin must be sought in very deep zones of the atomic structure.

The behaviour of the ionizing potentials tells us that the external electronic shell is the same for all these elements, with the possible exception of cerium, in agreement with the results of long and tiresome studies of the chemical properties.

We have found the absolute values of the potentials for the rare earths to be rather small, varying from 5·49 to 7·06 volts, in good agreement with the strong basic character of these elements.

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XXXII. *The Crystal Structure of Nickel.* *By* L. MAZZA and A. G. NASINI *.

[Plate IV.]

THE crystal lattice of nickel has been determined by different authors, but with somewhat divergent results. According to Hull's (1) first determinations, nickel exists both in face-centred cubes and in body-centred faces, the lattice constant of the face-centred form being 3·54 Å. (2).

* Communicated by Prof. T. M. Lowry, F.R.S.

Other authors have observed only the face-centred form, and have given for the edge of the elementary cube values ranging from 3·499 to 3·54 Å., as set out in Table I.

The difference of 0·04 Å. between the recent values of Sacklowski and of Davey is not easy to explain, in view of the exactness of modern X-ray technique, which permits of readings to 0·001 Å. by the powder method. On the other hand, the lattice dimensions of pure nickel are not likely to vary to this extent, in view of the satisfactory agreement reached with other metals; nor can these discrepancies be attributed to deformation of the lattice, because in this case characteristic features ought to be developed in the spectrograms. Finally, a critical review of the data is rendered impossible by the absence in certain cases of experimental details as to the preparation and diameter of the sample, and also the distance between sample and anticathode.

TABLE I.

Lattice constant.	Authorities.
3·499 ± 0·003 Å.	Davey, Phys. Rev. xxvii. p. 292 (1924).
3·51	F. Wever, *Mitt. Kaiser Wilhelm Inst. Eisenforsch*, iii. p. 17 (1922). McKeehan, Phys. Rev. xxi. p. 402 (1923).
3·518	H. Lange, *Ann. d. Phys.* lxxvi. pt. 4, p. 476 (1925).
3·52	S. Holgerson, *Ann. der Phys.* lxxix. pt. 1, p. 35 (1926).
3·53	H. Bohlin, *Ann. d. Phys.* lxi. p. 421 (1920).
3·536	G. L. Clark, W. G. Ashbury, and R. M. Wick, Journ. Am. Chem. Soc. p. 2661 (1925).
3·54	A. W. Hull, *loc. cit.* A. Sacklowski, *Diss. Greifswald* (1924).

The present experiments had their origin in an extended series of X-ray analyses by one of us (L. Mazza) of the nickel-copper alloys, in the course of which a number of samples of nickel were examined, with concordant results. We therefore thought it useful to make a complete series of exact experiments, with special precautions as to the purity of the samples, the possible influence of thermal and mechanical treatment, and the precision of the methods used to determine the lattice dimensions.

Experiments were also made to determine whether nickel can show at ordinary temperatures *, in addition to the face-centred form, the body-centred form recorded by Hull(1).

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* In another paper we will report about the structure of nickel at high temperatures.

The following methods of preparation were used *:—

(1) *Electrolytic Deposition.*—The bath, already used successfully in other researches ⁽³⁾, had the following composition: $NiSO_4 . 7H_2O$, 40 g. ; NH_4Cl, 20 g.; citric acid, 2 g.; water 1000 c.c. The nickel was deposited with a current-density of 0·003 amp. per cm.^{2} on a very thin wire (0·2 mm. diam.) of the same metal ; in this way nickel wires of 1 mm. diam. were obtained.

With the radiations used by us the diffraction takes place in a very thin surface-layer ; the internal core of drawn nickel wire has no influence on the results.

(2) *Reduction of the Oxide by heating in a Current of Hydrogen.*—The product was obtained as a light grey powder of metallic aspect. Nickel oxide was heated in a current of hydrogen at 600° C. during a period of 4 hours, when the reduction was practically complete.

(3) *Decomposition of Nickel Carbonyl.*—A thin plate of nickel formed by decomposition of $Ni(CO)_4$ on a hot metal plate was cut into strips about 3 mm. wide. These were bent very carefully (in order to avoid mechanical deformation) into hollow cylinders of 1 mm. diam.

Samples of pure commercial nickel were also examined which have been drawn by us in a steel wire-drawing machine to 1 mm. diameter. Some of them were further examined after rolling in a small rolling machine with steel cylinders, or after cold wire-drawing and also after prolonged annealing in a current of pure dry hydrogen in an electric furnace with a porcelain tube, followed in some instances by quenching in cold water. The annealing temperatures were controlled, and kept constant at 940° or 1200° C., by a thermocouple and a regulating resistance ; the annealing and quenching temperatures are tabulated for each sample ; time of annealing was usually 10 hours, but in one case it was extended to 30 hours.

The measurements were made by the method of Debye and Hull, with the following special features : the use of a new X-ray tube, regulated to give a very small surface of the local point upon the anticathode (4); maintaining a constant known distance between this focal point and the sample; the use of a precision spectrographic camera with diaphragms of accurately-calibrated dimensions. It was therefore possible to apply a correction for the divergence of the X-ray pencil, and to make use of the most accurate methods for determining the lattice constants from precision photograms (5).

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* The method of preparation by cathodic deposition has not been used on account of the difficulty of obtaining the metal in a massive state. Recently Bredig and Allolio (*Zeitschr. f. phys. Ch.* cxxvi. p. 41, 1927) have examined some samples of nickel cathodically deposited in an atmosphere of hydrogen at a few tenths of a millimetre of pressure. These seemed to have a close-packed hexagonal structure.

A precision camera of great mechanical rigidity was used with a cylindrical film supporter of 57·3 mm. diam.

The film was attached closely to the film-supporter as to allow of comparable measurement with different samples.

The samples, in the form of cylindrical rods of about 1 mm. diam., were held in such a way that the axis of the rod always coincided with that of the film supporter.

The Röntgen tube, made in the laboratory workshop, was of the metallic type of Hadding, modified by the replacement of the afflux cathode by an electron cathode (Coolidge) and cooling devices (4). The copper anticathode was excited with an alternating current of 60 k.v. max. and 15 m.a. intensity.

The distance between the centre of the spectrographic camera and the centre of the anticathode was 10 cm. In these conditions good photograms could be obtained with an exposure of 2½ hours.

The photogram obtained with electro-deposited nickel (without any further thermal or mechanical treatment) (Pl. IV. fig. 1) shows only nine diffraction lines, all derived from Kα doublet of copper (mean value of $1 = 1{\cdot}539 \times 10^{-8}$ cm.). The lines are narrow and regular, from which we may infer that the electro-deposited nickel is not oriented, but consists of very small grains, though not of comparable size.

The results of the determination are recorded in Table II. In the first column, under "$\frac{\theta}{2}$," are recorded the values in degrees and minutes of the angles of each diffraction line, corrected in the usual way for the displacement due to the diameter of the preparation (1 mm.) and the divergence of the X-ray (diameter of diaphragm 1·2 mm., distance between sample and anticathode 10 cm.). In the second column are tabulated the corresponding sines; in the third, Miller's indices; in the fourth, the ratio

$$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2};$$

in the fifth and sixth, those measured by a microphotometer and calculated by the formula:

$$I = N\left(\frac{d_{hkl}}{n}\right)^{2\cdot 35}(A^2+B^2)$$

(where N represents the number of planes of the crystal considered as co-working to the formation of each line and (A^2+B^2) is the phase factor) for the following position of the atoms:

$$0\,0\,0;\ \tfrac{1}{2}\,\tfrac{1}{2}\,0;\ \tfrac{1}{2}\,0\,\tfrac{1}{2};\ 0\,\tfrac{1}{2}\,\tfrac{1}{2}.$$

Finally, in the last column are tabulated the number N of planes co-operating in the formation of each line.

To calculate the lattice constant "a" we have taken into account (6), in deducing the mean value of the expression

$$X = \frac{\left(\sin^2\frac{\theta}{2}\right)}{h_1^2+h_2^2+h_3^2},$$

that each single measurement must be evaluated in relation to its certainty, according to Gauss's law of observation errors. Since, in the present instance, the "weight" is proportional to $\tan^2\frac{\theta}{2}$, the mean value X_0 is expressed by

$$X_0 = \frac{\Sigma X \tan^2\frac{\theta}{2}}{\Sigma \tan^2\frac{\theta}{2}}.$$

The limit of error for the length of the side of the elementary cube is then given by

$$\Delta a = \tfrac{1}{2}\,\frac{\sqrt{\dfrac{\left((X-X_0)\tan^2\frac{\theta}{2}\right)^2}{(n-1)\tan^2\frac{\theta}{2}}}}{X_0}\cdot \dot{a},$$

and the value of the lattice constant is then

$$a = \dot{a}_0 \pm \Delta a,$$

where

$$\dot{a}_0 = \frac{\lambda}{2\sqrt{X_0}}.$$

In calculating the values of the lattice constant and the limits of error, we have omitted the datum corresponding approximately to the 78·5° line. This line, as is usually the case when the deviations are large, appears very shaded in all photograms, and is not suitable for an exact measurement on the comparator.

Since we could not rely upon getting values of a precision comparable with that obtainable with smaller angles, we thought it better not to use this line for the present calculations.

TABLE II.

Electrolytic Nickel Wire.

1 mm. diam. Diameter of the cylinder supporting the film, 57·3 mm. Copper radiations, Cu Kα = 1·539 Å. Exposure, 2000 milliamp. minutes.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$.	$h_1\,h_2\,h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I. Obs.	I. Calc.	N.
22° 19′	0·3797	1 1 1	0·04806	ff.	100	8
26 0	0·4384	0 0 2	0·04806	f.	54	6
38 17	0·6196	2 0 2	0·04798	f.	47	12
46 32	0·7258	1 1 3	0·04790	f.	65	24
49 20	0·7585	2 2 2	0·04794	d.	19	8
61 14	0·8766	0 0 4	0·04802	d.	10	6
72 37	0·9543	3 1 3	0·04793	f.	33	24
78 5	0·9784	2 0 4	0·04787	f.	32	24

$a = 3{\cdot}514 \pm 0{\cdot}001$ Å.
$d = 8{\cdot}925$.

From this value of "*a*" is calculated the density :

$$d = \frac{4 \times 58{\cdot}68 \times 1{\cdot}650 \times 10^{-24}}{(3{\cdot}514 \times 10^{-8})^3} = 8{\cdot}925.$$

The samples of nickel prepared by reduction from the oxide were tested by putting the powdered nickel in small tubes of paraffined paper of 1 mm. diam., using the same method as for electrolytic nickel. A photogram is shown in fig. 2 (Pl. IV.) and the relevant data are set out in Table III.

The length of the edge of the elementary cube is within 0·001 Å. of that of nickel obtained by electrolytical deposition.

TABLE III.

Nickel reduced from the Oxide.

Diameter of the sample, 1 mm. Diameter of the cylinder supporting the film, 57·3 mm. Copper radiations, Cu Kα = 1·539 Å. Exposure, 2000 milliamp. minutes.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$.	$h_1\ h_2\ h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.		N.
				Obs.	Calc.	
22° 17′	0·3792	1 1 1	0·04793	ff.	100	8
25 57	0·4376	0 0 2	0·04787	f.	54	6
38 15	0·6191	2 0 2	0·04791	f.	47	12
46 30	0·7254	1 1 3	0.04783	f.	65	24
49 19	0·7583	2 2 2	0·04792	m.	19	8
61 12	0·8763	0 0 4	0·04800	d.	10	6
72 36	0·9542	3 1 3	0·04793	f.	33	24
78 3	0 9783	2 0 4	0·04785	f.	32	24

$a = 3·513 \pm 0·001$ Å.
$d = 8·918$.

TABLE IV.

Nickel from the Carbonyl.

Diameter of the sample, 1 mm. Diameter of the cylinder supporting the film, 57·3 mm. Copper radiations, Cu Kα = 1·539 Å. Exposure, 2000 milliamp. minutes.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$.	$h_1\ h_2\ h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.		N.
				Obs.	Calc.	
22° 19′	0·3797	1 1 1	0·04806	ff.	100	8
26 0	0·4384	0 0 2	0·04804	f.	54	6
38 17	0·6196	2 0 2	0·04798	f.	47	12
46 34	0·7262	1 1 3	0·04805	f.	65	24
49 21	0·7587	2 2 2	0·04797	d.	19	8
61 15	0·8767	0 0 4	0·04804	d.	10	6
72 38	0·9544	3 1 3	0·04794	f.	33	24
78 6	0·9785	2 0 4	0·04787	f.	32	24

$a = 3·513 \pm 0·001$ A.
$d = 8·933$.

Nickel obtained from $Ni(CO)_4$ was examined in small hollow cylinders of 1 mm. external diameter prepared as already mentioned, avoiding all mechanical work capable of producing a deformation in the structure of the samples.

The reproduction of a photogram is given in fig. 3 (Pl. IV.), whilst the relevant data and the results of the mechanical calculations are set out in Table IV.

In this case again the length of the edge does not differ appreciably from the preceding values.

Table V.

Commercial nickel wire of 1 mm. diameter. Diameter of the cylinder supporting the film, 57·3 mm. Copper radiations, Cu Kα = 1·539 Å. Exposure, 2000 milliamp. minutes.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$.	$h_1\,h_2\,h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.		N.
				Obs.	Calc.	
22° 19′	0·3797	1 1 1	0·04806	ff.	100	8
26 0	0·4384	0 0 2	0·04804	f.	54	6
38 15	0·6191	2 0 2	0·04791	f.	47	12
46 35	0·7264	1 1 3	0·04797	f.	65	24
49 21	0·7587	2 2 2	0·04797	d.	19	8
61 16	0·8769	0 0 4	0·04805	d.	10	6
72 39	0·9545	3 1 3	0·04795	f.	33	24
78 7	0·9786	2 0 4	0·04788	f.	32	24

$a = 3{\cdot}510 \pm 0{\cdot}001$ Å.
$d = 8{\cdot}956$.

One of the spectrograms obtained with pure commercial nickel in cold-drawn wires of 1 mm. diam. is shown in fig. 4 (Pl. IV.); data and calculations are given in Table V.

It is remarkable that the photograms of this sample do not show the characteristics of a wire-drawing structure.

Table VI. shows the date for a similar sample after being annealed for 10 hours at 940° C.

The photogram does not differ appreciably from that of the same nickel when not annealed after cold drawing.

The diffraction lines are very narrow and do not show any trace of recrystallization.

The length of the edge of the elementary cell differs from that of the unannealed sample only by 0·004 Å.

Another sample of the same cold-drawn nickel was annealed during 30 hours at 1200° C. It showed under the microscope (with small magnification) the formation of large crystals.

A rough examination of the mechanical properties showed a remarkable diminution of ductility and a very low value for the tensile strength.

TABLE VI.

Diameter of the sample, 1 mm. Diameter of the cylinder supporting the film, 57·3 mm. Copper radiations, Cu Kα = 1·539 Å. Exposure, 2000 milliamp. minutes.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$	$h_1 h_2 h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.	I.		N.
				Obs.	Calc.	
22° 19′	0·3797	1 1 1	0·04806	ff.	100	8
25 59	0·4381	0 0 2	0·04798	f.	54	6
38 17	0·6196	2 0 2	0·04798	f.	47	12
46 31	0·7256	1 1 3	0·04786	f.	65	24
49 21	0·7587	2 2 2	0·04797	d.	19	8
61 13	0·8765	0 0 4	0·04801	d.	10	6
72 38	0·9544	3 1 3	0·04794	f.	33	24
78 6	0·9785	2 0 4	0·04787	f.	32	24

$a = 3{\cdot}514 \pm 0{\cdot}001$ A.
$d = 8{\cdot}925$.

The photogram of this sample is given in fig. 5 (Pl. IV.). It shows clearly that annealing has given rise to a coarse-grained structure with a somewhat regular orientation.

There is also an almost complete absence of interference lines of the characteristic type which one gets from irregularly-oriented crystal particles having dimensions inferior to 1×10^{-2} mm., but larger than colloidal particles. The position of the single interference lines coincides accurately with the position of the lines of the previous photograms.

Some of the samples used in the three preceding experiments were subjected, after annealing, to a rapid cooling (quenching). The photogram of a sample annealed for 10 hours at 940° C. and quenched from the same temperature is identical with the one of the unannealed sample.

A sample subjected to the same thermal treatment at 1000° C. gave a very different X-photogram (Pl. IV. fig. 6). One may easily detect the appearance of a recrystallization structure with irregular orientation, and this structure seems to be superposed on the pre-existing structure, whose type is that required for small crystal particles with completely irregular orientation. Notwithstanding the appearance of recrystallization the photogram shows some very narrow lines from which the lattice constant can be determined as in Table VII.

TABLE VII.

$\frac{\theta}{2}$ corrected.	$\sin\frac{\theta}{2}$.	$h_1\, h_2\, h_3$.	$\frac{\sin^2\frac{\theta}{2}}{h_1^2+h_2^2+h_3^2}$.
22° 18′	0·3794	1 1 1	0·04799
26 0	0·4384	0 0 2	0·04804
38 16	0·6193	2 0 2	0·04795
46 30	0·7254	1 1 3	0·04783
49 18	0·7581	2 2 2	0·04790
61 13	0·8765	0 0 4	0·04801
72 37	0·9543	3 1 3	0·04793
78 5	0·9905	2 0 4	0·04787

$a = 3{\cdot}514 \pm 0{\cdot}001$ Å.
$d = 8{\cdot}925$.

We thus find that samples of nickel which have been annealed for a long time and afterwards quenched show only a face-centred cubic structure, and that the dimensions of the elementary cell seem to have changed very little.

Conclusions.

(1) Nickel obtained (a) *by electrolytic deposition*, (b) *by separation from* $Ni(CO)_4$, (c) *by reduction of the oxide* crystallizes in face-centred cubes. The dimensions of the crystal particles range from 1×10^{-2} to 1×10^{-6} cm.

(2) The length of the edge of the elementary cell ranges from 3·513 ± 0·001 Å. to 3·515 ± 0·001 Å.

The mean value for samples of normal structure is 3·514 ± 0·002 Å., in close agreement with the values of Wever, of McKeehan, and of Lange (see Table I.).

(3) Pure cold-drawn nickel, after various thermal treatments, although sometimes showing peculiar recrystallization, always crystallizes in face-centered cubes. No confirmation has been found of Hull's observation of the existence of nickel crystallizing at ordinary temperature in body-centered cubes. The length of the edge of the elementary cube differs but little from that determined for the previous samples.

(4) Pure cold-drawn nickel subsequently annealed for a long time does not show recrystallization structures, detectable by X-ray analysis, for annealing temperatures up to 940° C. The appearance of characteristic recrystallization structures is only observed at temperatures of 1000° C. and above. Prolonged annealing (30 hours) at 1200° C. produces a recrystallization in coarse grains, irregularly oriented, giving rise to a marked reduction of properties such as ductility and tensile strengths.

(5) Quenching does not produce any change in the dimensions of the lattice of nickel.

(6) The relative intensity of the various lines is approximately the same in the photograms of all samples examined, and is in good agreement with the values deduced by means of the approximate formula adopted in the present calculations.

We wish to thank the Mond Nickel Co., Ltd., who presented us with some samples of pure nickel, and Dr. B. Nuterini for her help in the experimental work.

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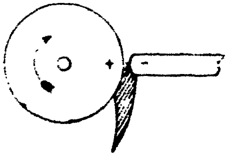
XXXIII. *On the Influence of a Hydrogen Atmosphere upon the Arc Spectra of Certain Metals.* *By* HENRY CREW [*].

1. MORE than a quarter of a century ago, I described, in this Magazine [†], some marked changes in the line spectra of magnesium, zinc, and iron when the air surrounding the electric arc which furnishes the light is replaced by an atmosphere of hydrogen. The arc employed at that time was produced by 100 volts acting between a fixed electrode made of the metal in question and a rapidly rotating electrode in the form of a disk made of the same metal. This arc was enclosed in an insulated brass case, so that a current of air flowing through the hood could be replaced by a stream of hydrogen gas without changing anything else about the entire apparatus. Corresponding to this change of atmosphere certain differences in the spectra were observed. The hydrogen introduced asymmetrical shading, changes in reversal, and marked alteration in intensity, sometimes greatly increasing the strength of a line, sometimes causing it almost to vanish. In general the spark lines were found to be most sensitive to hydrogen, and lines belonging to the principal and diffuse series were practically immune.

2. The explanation of most of this effect, which seemed to be entirely out of proportion to its cause, occurred to me only a few weeks ago. It is as follows. In using the arc, which has a rotating disk for one electrode, the image of the arc on the slit of the spectroscope is something like that



indicated by the shaded portion of the accompanying figure. Naturally one sets the brightest portion of this "flame" of luminous vapour on the slit; and, in air, this is the central portion. In hydrogen, however, one finds that the "flame" contracts to a mere fraction of its size in air, and recedes to a small luminous spot in the angle between the fixed and moving electrodes. Under these circumstances again one naturally puts the brightest part of the spot on the slit, and this means that the source of light illuminating the slit is very near each of the poles. The result of the use of a hydrogen atmosphere is therefore to introduce what is known as "pole-effect." I was therefore mistaken in thinking that, on introducing hydrogen, I was changing only one independent variable. The principal pole-effect considered during the past twenty years has been a change of wave-length; but there are several other effects of this same cause which are easily seen by photographing the entire length of the arc in a spectrograph which is not astigmatic. Among these other effects the principal ones are the three mentioned above—namely, asymmetrical shading, reversal, and change of intensity.

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[*] Communicated by the Author.

[†] Phil. Mag. l. p. 497 (1900).

It is generally believed, I suppose, that these effects are produced by the steep potential gradient (Stark effect), the change of temperature, and the change of vapour density which are met with in a close approach to either pole of the arc. In addition to these effects, one can predict also that an atmosphere of hydrogen will introduce certain chemical effects, such, for example, as the quenching of the cyanogen bands in the carbon arc, and the exclusion of the magnesium oxide bands when magnesium poles are used; also the introduction of bands due to metallic hydrides; and, what perhaps might *not* be expected in the arc, the appearance of the lines H_β, H_γ, H_δ.

3. In order to eliminate these pole-effects, and to discover the *bona fide* consequences of a hydrogen atmosphere, two methods were employed. The first consisted in using fixed electrodes in a water-jacketed chamber and *keeping the arc-length the same in air as in hydrogen.* This is not easy to do, since most arcs are maintained in hydrogen at ordinary barometric pressure only with difficulty; and this is true even when four or five hundred volts are employed. In this method the images of the two poles each lie on the slit.

The second and better method is the use of a vertical arc, projected upon the slit of the spectrograph by means of the ordinary quartz image-lens *and a reversing prism*, this latter being placed close in front of the slit. In this manner the image of the arc on the jaws of the slit lies at right angles to the slit; the image of neither pole lies on the slit; so that when the arc is maintained at constant length, the only effect, if any, which one gets, on surrounding the arc with hydrogen, is that due to hydrogen alone. Any pole-effect is thus eliminated. The spectra of Zn, Cu, Cd, Mg, Al, and C, between λ 5000 and λ 3700 have recently been photographed in this manner; and by use of the first method, where no glass is involved, the same spectra have been photographed between λ 5000 and λ 2200.

4. The purpose of this note is to describe a few typical spectral appearances which do *not* seem to be pole-effects.

The Spectrum of Magnesium.

Here the widening of the reversal does not always appear to be a pole-effect. This is notably true of the singlet λ 2852, where the width of reversal at the pole, in air, is approximately *one* Ångström unit, while in hydrogen it is more nearly *five* Ångströms in width. The singlet at λ 4571 is, on the contrary, quite unaffected by hydrogen.

The diffuse triplets at $\lambda\left\{\begin{matrix}2851\cdot6\\2848\cdot4\\2846\cdot7\end{matrix}\right\}$ and $\lambda\left\{\begin{matrix}2736\cdot5\\2733\cdot5\\2732\cdot0\end{matrix}\right\}$ are practically blotted out in hydrogen; while the sharp triplet $\lambda\left\{\begin{matrix}2942\cdot1\\2938\cdot5\\2936\cdot8\end{matrix}\right\}$ is greatly weakened. The copper impurities at $\lambda\left\{\begin{matrix}3273\cdot964\\3247\cdot548\end{matrix}\right\}$ are relatively much weakened, but are still visible in hydrogen, in spite of the fact that each shows a distinct increase of intensity near the pole, in both the long and the short air arc. The calcium impurity at $\lambda\left\{\begin{matrix}3968\cdot475\\3953\cdot670\end{matrix}\right\}$ is weakened just as the copper; but the aluminium pair $\lambda\left\{\begin{matrix}3961\cdot537\\3944\cdot670\end{matrix}\right\}$ is practically unchanged in passing from air to hydrogen.

The Spectrum of Zinc.

The singlet, λ 4298·4, is practically blotted out by hydrogen. The ubiquitous copper impurities $\lambda\left\{\begin{matrix}3273\cdot9\\3247\cdot5\end{matrix}\right\}$ are here also reduced to a mere trace of what they are in air. So also is the diffuse singlet, at λ 4629·8. But the triplet of the sharp series $\lambda\left\{\begin{matrix}4810\cdot5\\4722\cdot1\\4680\cdot2\end{matrix}\right\}$ is almost unaffected by hydrogen.

The Spectrum of Aluminium.

The outstanding difference between the aluminium arc in these two atmospheres is the appearance, in hydrogen, of a strong and open band with heads at λ 4241, λ 4259, λ 4353, of which no trace is found in air. This aluminium hydride band appears to have been first observed by Basquin *, studied by Eriksson and Hulthén †, and interpreted by Mulliken ‡.

As to impurities, the strong and almost omnipresent lead line at λ 4057·830 and the manganese lines at $\lambda\left\{\begin{matrix}4034\cdot489\\4033\cdot074\\4030\cdot760\end{matrix}\right\}$ come out very clearly in hydrogen, while they are barely visible in air. The diffuse zinc triplet, at $\lambda\left\{\begin{matrix}3345\cdot\\3302\cdot\\3282\cdot\end{matrix}\right\}$, is also brought out in hydrogen; while the merest trace of it appears in air. In contrast with this, the unfailing copper impurity at $\lambda\left\{\begin{matrix}3273\cdot964\\3247\cdot548\end{matrix}\right\}$ is equally strong in air and in hydrogen.

The Spectrum of Cadmium.

The only striking change in passing from air to hydrogen is the introduction of an enormous number of impurity lines between λ 5000 and λ 3200. Curiously enough, the lead line at λ 4057·8 comes out clearly in air while no identification of it is easily made among the multitude of foreign lines which record themselves in hydrogen. This behaviour of the lead line, it will be observed, is just the reverse of what happens in the aluminium arc.

The Spectrum of Carbon.

Here the only thing which one might not easily predict is the appearance of a fluting with a head at λ 4313, and extending towards the shorter wave-lengths. Other less prononnced bands are introduced in the neighbourhood of λ 3142 and λ 3155. Again, the hydrogen atmosphere blots out many impurities, such as Fe $\left\{\begin{matrix}3440{\cdot}991\\3440{\cdot}612\end{matrix}\right\}$ and Si, 2881·587, while it intensifies the carbon spark line at λ 2478·6 and brings out strongly H_β and H_γ.

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* Astrophys. Journ. xiv. p. 8 (1901).

† *Zeits. f. Physik*, xxxiv. p. 775 (1925).

‡ Phys. Rev. xxviii. p. 1207 (1926).

5. It is not unlikely that, if electrodes different from the few mentioned above were used, a hydrogen atmosphere would produce other spectral changes worthy of study. Just how a cause so gentle and feeble as a change of atmosphere around a storm-centre such as an electric arc carrying several amperes at ordinary barometric pressure can produce such marked alterations in the spectrum, is not easy to understand.

If one accepts the Bohr theory of radiation one is confronted with the problem of explaining how a hydrogen atmosphere can affect the ionization of the atom and how it can change the programme of an electron in falling back through various levels. Professor W. F. G. Swann has suggested that, since the molecule of hydrogen gas has a root-mean-square speed four times as great as that of oxygen or nitrogen, the number of collisions in a mixture of hydrogen and metallic vapour must be greater than in air; and hence the probability of certain electron-jumps may be increased, thus increasing the intensity of certain lines. It has also been suggested by Professor W. R. Ham that the reason copper impurities are weakened in hydrogen is that the "work function" for the positive copper ion is greater in an atmosphere of hydrogen than in an atmosphere of air; but just how this can come about is not clear. The striking temperature effects which Langmuir * obtained by directing a jet of hydrogen from a small tube into an electric arc leads one to think that a hydrogen atmosphere may not perhaps be such a mild agent as one may at first imagine it.

The conclusion of this note is, then, the description of certain phenomena which are introduced by an atmosphere of hydrogen, but which do not appear to be explicable as "pole-effects."

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September 3rd, 1928.

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* 'Science,' lxii. pp. 463–464 (1925).

XXXIV. *On the Hydrolytic Adsorption by Humic Acid.* By ASHUTOSH GANGULI, *Lecturer in Chemistry, Serampore College, Bengal*[*].

MICHAELIS and Rona[†], in their classical work on the adsorption of electrolytes by blood charcoal, have estimated the adsorption of cations as well as anions, and found a regular order for these. During recent years Mukherjee and his co-workers[‡] have investigated a certain class of substances which liberate free acid when shaken with neutral solutions of electrolytes. This phenomenon is now known as hydrolytic adsorption.

According to Freundlich[§] the adsorbents which adsorb electrolytes polarly are probably amorphous solid electrolytes with one sluggish ion and one mobile ion. The more strongly adsorbed ion has a tendency to go to the interface and drags along with it the more weakly adsorbable ion in part to the interface, while the latter ion holds back the former in the solution[‖]; thus an equilibrium is set up. In some cases, however, the ionic adsorption is accompanied by exchange-adsorption or hydrolytic decomposition.

Recently, in 1922, Mukherjee[¶] extended the electrical theory of adsorption of Freundlich, and explained the general nature of hydrolytic adsorption. According to him a particular ion penetrates the interface and enters within the double layer, forming a heavy "sluggish" ion, while the opposite ion is held by electrical attractive force in the mobile sheet of the double-layer. This mobile ion, if it happens to be an anion, can be exchanged for (OH) obtained from the dissociation of water, and pass into solution in the free state, thereby causing the liberation of acid. Thus the ionization of water into $H^{\cdot}$ and $(OH)'$ and the exchange of ions go on until equilibrium is attained, when all the ions in the mobile sheets have been replaced by H or $(OH)'$. Joseph and Hancock[**], on the other hand, believe that the liberation of acids by shaking electrolytes with substances like silica is entirely chemical in nature, due to the formation of insoluble silicates. In a recent paper [*] on the hydrolytic adsorption by chemically pure silica, Mukherjee and his co-worker have contradicted this view. Again, in a more recent paper Hahn [†] points out the existence of a relationship beween the adsorption of a radio element by a polar precipitate and the electric charge at the surface, and thus confirms the contention of Mukherjee.

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[*] Communicated by Prof. K. C. Kar.

[†] *Biochem. Zeitschrift*, xciv. p. 240 (1914).

[‡] Journal of Ind. Chem. Soc. i. p. 191 (1925); *ibid.* iii. p. 371 (1926); *ibid.* iv. p. 458 (1827); J. C. S. cxxiii. pp. 2205, 3023 (1926); also Miller, Journ. Am. Chem. Soc. xlvi. p. 1150 (1924); Bartell & Miller, *ibid.* lxv. p. 1106 (1923).

[§] 'Kapillarchemie' (Eng. Edn.), p. 207.

[‖] *Ibid.* p. 212.

[¶] Phil. Mag. xliv. (6) p. 330 (1922); *loc. cit.*

[**] J. C. S. cxxiii. p. 2022 (1923).

"The adsorptive properties of humin for substances in solution is of great importance in agriculture" [‡]. Russell [§] points out that neutral solutions of salts like KCl, if treated with samples of soils, give acid extract, though the extract with pure water is neutral. It has been suggested by Mukherjee [||] that the acidity of soils can be explained in the light of hydrolytic adsorption. Recently Kawamura [¶] performed some experiments with the synthetic humic acid. The present work has been undertaken in order to examine the nature of hydrolytic adsorption by humic acid, and thus explain the acidity of soils.

Experimental.

Kahlbaum's pure sample of humic acid was analysed, and was subsequently used in the following experiments:—1 gm of humic acid was taken in a Jena bottle and shaken in a mechanical shaker with 100 c.c. standard solutions of the electrolytes at different concentrations. This was allowed to stand for two or three days. The clear supernatant liquid was then transferred by means of a pipette in a well-cleaned dry hydrogen cell, and a very slow current of hydrogen was bubbled through it for more than two hours. The e.m.f. of this was determined against a normal calomel electrode by means of a K-type potentiometer (Leeds & Northrup). The concentration of hydrogen-ion C_H was calculated from the well-known equation

$$E = e_0 + \frac{RT}{nF} \log \frac{c_1}{c_2}$$

or

$$E - e_0 = \frac{RT}{nF} \log \frac{1}{C_H} = \cdot 059\ P_H.$$

e_0 is the absolute value of the electrolytic potential of hydrogen measured against “normal” calomel electrode, E is the observed e.m.f., and $P_H = \log \frac{1}{C_H}$, where C_H = concentration of H-ion.

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[*] *Loc. cit.*

[†] *Ber.* lix. p. 2014 (1926).

[‡] 'A Manual of Agricultural Chemistry' (Ingle).

[§] British Assoc. Report, p. 70 (1918).

[||] *Loc. cit.*

[¶] Journ. Phys. Chem. xxx. p. 1564 (1926).

TABLE I.

1 gm. of Humic acid 100 c.c. NaCl solution.

T=28·5.

Concentration of NaCl gm.-equivalents per litre.	P_H.	$C_H\ 10^{-4}$.
1·00	3·35	4·467
0·5	3·42	3·802
0·25	3·51	3·090
0·1	3·62	2·399
0·000	4·56	0·2754

TABLE II.

1 gm. of Humic acid in c.c. KCl solution.

T=35° C.

Concentration of KCl gm.-equivalents per litre.	P_H.	$C_H\ 10^{-4}$.
2·00	2·19	64·57
1·00	2·799	15·89
0·50	3·06	8·710
0·25	3·19	6·457
0·100	3·61	2·455
0·025	4·05	0·8913
0·005	4·48	0·3311
0·000	4·56	0·2754

TABLE III.

1 gm. of Humic acid in 100 c.c. $BaCl_2$ solution.

T=35° C.

Concentration of $BaCl_2$ gm.-equivalent per litre.	P_H.	$C_H 10^{-4}$.
1·000	2·64	22·91
0·500	3·00	10·00
0·100	3·02	9·55
0·050	3·21	6·166
0·025	3·23	5·188
0·010	3·41	3·890
0·005	3·6	2·512
0·000	4·56	0·2754

TABLE IV.

1 gm. of Humic acid in 100 c.c. $AlCl_3$ solution.
T=35° C.

Concentration of $AlCl_3$ gm.-equivalent per litre.	P_H.	C_H 10^{-4}.
1·000	2·28	52·48
0·500	2·28	52·48
0·250	2·33	46·77
0·100	2·66	21·88
0·050	2·66	21·88
0·025	2·77	16·98
0·010	2·95	11·22
0·000	4·56	0·2754

TABLE V.

1 gm. of Humic acid in 100 c.c. K_2SO_4.
T=35° C.

Concentration of K_2SO_4 gm.-equivalent per litre.	P_H.	C_H 10^{-4}.
1·000	4·00	1·000
0·500	3·73	1·862
0·250	3·99	1·023
0·100	4·00	1·000
0·050	3·83	1·479
0·025	3·93	1·175
0·010	4·02	0·9550
0·000	4·56	0·2754

TABLE VI.

1 gm. of Humic acid in 100 c.c. of normal solutions of various electrolytes.

	Water.	NaCl.	KCl.	$BaCl_2$.	$AlCl_3$.	K_2SO_4
P_H	4·56	3·35	2·799	2·64	2·28	4·00
$C_H 10^{-4}$ ...	0·2754	4·467	15·89	22·91	52·48	1·00

Discussion of Results.

From the foregoing tables it will be observed that the concentration of hydrogen ion, and hence the amount of free acid liberated, varies directly with the concentration of the electrolyte. As has been observed in the introduction, the liberation of the free acid is due to the adsorption of cations by the humic acid particles to form a complex electrolyte. Thus the cation is fixed within the double layer, whereas the anion, which is held by electrical attraction in

§ 4. *The Vibrations of a Rectangular Plate clamped at the Edges.*

The process mentioned in the last paragraph gives a ready solution of the problem of the flexural vibrations of a thin rectangular plate clamped at the edges. Assuming simple harmonic vibrations of period $2\pi/\sigma$, the equation * to be solved in place of (1) is

$$\frac{\partial^4 w}{\partial x^4}+2\frac{\partial^4 w}{\partial x^2\partial y^2}+\frac{\partial^4 w}{\partial y^4}-\lambda w=0, \quad . \quad . \quad . \quad (18)$$

together with the conditions (2) as before.

Assuming the expansion for w, as in (14) substituting and reducing by means of (12), the resulting algebraic expression is

$$a_{mn}\{(\kappa_m/a)^4+(\kappa_n/b)^4-\lambda\}+2\sum_r\sum_s a_{rs}\sigma_{rm}\sigma_{sn}/a^2b^2=0. \quad (19)$$

The equation (19) holds for all values of m, n, and represents a doubly-infinite series of equations each containing a doubly-infinite number of terms. The eliminant of the set gives an equation in λ, the various roots of which correspond to the normal modes of vibration.

The equations (19) may be solved and the normal modes obtained exactly as was done by Ritz for the corresponding problem of the vibrations of a plate with free edges †.

XXXVII. *Temperature Coefficient of Gamma-Ray Absorption.* By L. Bastings, *M.Sc.*, *F.Inst.P.* ‡

OWING to recent improvements in the methods and technique of γ-ray measurements with a gold-leaf electrometer §, γ-ray absorption constants can now be determined with sufficient accuracy to make possible an investigation into the effect of temperature on the absorption. Preliminary experiments carried out and briefly reported some two years ago ‖ established the fact that the atomic absorption increases with temperature; and in the present account, experiments are described on a number of typical metals, all of which show a definite increase in this constant with rise of temperature.

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* Love, 'Elasticity,' p. 496.

† Ges. Werke, p. 292.

‡ Communicated by Sir E. Rutherford, O.M., P.R.S.

§ Bastings, J. Scient. Instr. v. p. 113 (1928).

‖ Bastings, 'Nature,' cxix. p. 51 (1927).

No previous attempt at this problem seems to have been made; but while the preliminary experiments were in progress, some similar results were published by Read*, dealing with the absorption of X-rays in the metals Al, Fe, Ni, Cu, Ag, and Pb. On raising the temperature, he found that, when due allowance had been made for the thermal expansion of the absorber, there remained in every case a small increase in the atomic absorption constant, amounting to about 0·2 per cent. per 100° C. up to temperatures near the melting-point of the absorber.

The Preliminary Experiments.

The first experiments were made with lead absorbers of about 17 cm. in diameter and 1·4 cm. in aggregate thickness. These could be inserted in a definite position in a tubular electric furnace 18 cm. in diameter and 50 cm. in length. The furnace was mounted between the source of γ-rays, a 10·37 mgm. tube of radium in equilibrium, and the gold-leaf electrometer, so that the absorber was 30 cm. from the source and 50 cm. from the centre of the electrometer. The temperature of the furnace was measured by a platinum resistance thermometer, inserted through a hole in the side, and the temperature was maintained constant to within 5° of 270° C. by hand regulation. Under these conditions the proportion of the rays absorbed by the screen decreased by about 0·4 per cent. per 100° C. rise in temperature; but when allowance was made for the expansion of the material, as explained below, the atomic absorption constant was found to increase by approximately 0·2 per cent. per 100° C. The measurements were sufficiently accurate to establish the existence of this increase; but no great reliance could be placed upon the magnitude deduced.

The New Experiments.

Accordingly a more suitable apparatus was designed. The furnace consisted of a quartz cylinder 38 cm. in length and 6·7 cm. in internal diameter, wound externally with nichrome strip and lagged in turn with alundum cement, kieselguhr, and asbestos wool. A temperature of about 1050° C. could be developed with 10 amps. at 100 volts. The temperature was measured by two chromel-alumel thermocouples inserted one in each end of the furnace, and resting almost in contact with the centre of the absorber when in its standard position. The junctions were read by a sensitive potentiometer, and were calibrated at four fixed points. Hand regulation was found adequate to maintain the temperature constant for several hours to within 1° at 500° and 2° at 1000°.

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* Read, Phys. Rev. xxvii. p. 373 (1926).

The escape of heat from the ends of the furnace was almost eliminated by a series of large asbestos screens, separated by air-gaps. And the electrometer was further thermally insulated by being enclosed almost completely in an asbestos box ; while heat from the source of illumination was eliminated by a cell containing a solution of ferrous ammonium sulphate. There was no evidence of the occurrence of any convection currents in the electrometer due to temperature gradients ; and, in fact, the temperature of the whole of the electrometer enclosure was almost independent of whether the furnace was on or off during an experiment.

The absorbers were cylindrical in shape and slightly smaller in diameter than the interior of the furnace. They could be accurately replaced in a standard position by the aid of a distance gauge. The radium was mounted on a geometrical stand, moving on an optical bench, and both this and the screen could be replaced with accuracy of two- or three-tenths of a millimetre. The solid angle subtended by the absorber at the source was a little more than adequate to include the whole of the electrometer within it.

Method of Measurement.

The general method of measurement was similar to that described in the previous paper [*]. The programme of observations consisted in taking ten timings of the leaf movement with each of the following dispositions :—

(*a*) furnace cold, absorber absent ;
(*b*) furnace cold, absorber present ;
(*c*) furnace hot, absorber present ;
(*d*) furnace hot, absorber absent.

The absorption constant at the lower temperature was deduced from (*a*) and (*b*), and at the higher temperature from (*c*) and (*d*). This procedure eliminates the effect of any extraneous change in absorption or scattering in and around the apparatus, as the result of the rise in temperature. The programme was repeated at least four times in each experiment; and ten experiments were performed with each absorber over every temperature range considered. The natural leak was measured before and after each series, and remained constant throughout the whole of the experiments at $0{\cdot}070 \mp {\cdot}002$ divisions per minute. Readings were of the order of from 14 to 35 divisions per minute, and it was seldom that the mean deviation from the average of ten readings was greater than 1 in 1000. The values of the absorption constants deduced could usually thus be relied on to 1 in 500, and the means to probably less than 1 in 1000.

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[*] Bastings, J. Scient. Instr. *loc. cit.*

Measurements were made with lead, iron, tin, and aluminium, and in addition, in the case of tin, the molten metal was employed in a cast-iron boat of special design. This boat, with its lid, was of cylindrical shape, and the rays were passed through it in a direction perpendicular to the parallel sides. The liquid enclosed subtended more than the requisite angle at the source. An exactly similar empty boat was used in a parallel set of control experiments.

Correction for Expansion.

A correction will have to be applied to the observations on account of the expansion of the absorber. This correction in the case of the liquid will be somewhat different from that in the case of the solid.

Consider the effect of raising the temperature of the absorber by $t°$ C. Suppose E and I represent the electrometer readings with and without the absorber at the lower temperature, and E′, I′ the corresponding readings at the upper temperature.

Let n be the number of atoms per c.c. in the absorber, μ the atomic absorption constant, and d the thickness of the absorber, all at the lower temperature, while dashed letters refer to the corresponding quantities at the upper temperature. Then

$$R = E/I = \exp(-n\mu d) \quad \text{and} \quad R' = E'/I' = \exp(-n'\mu'd').$$

Now, if α be the mean coefficient of linear expansion of the material of the absorber over the temperature range $t°$,

$$n = n'(1+\alpha t)^3$$

and

$$d' = d(1+\alpha t).$$

So

$$n\mu'd = n'\mu'd'(1+\alpha t)^2 = n'\mu'd'(1+2\alpha t),$$

approximately. Thus the increase in thickness of the absorber will have no direct effect on the absorption; but the increase in cross-sectional area removes from the path of the beam affecting the electrometer some of the atoms included in it at the lower temperature, and results in a decrease in the apparent absorption.

If, then, as we shall see, μ' is greater than μ, let us assume as a first approximation that the absorption constant has a linear temperature coefficient β over the range considered;

$$i.e., \qquad \mu' = (1+\beta t).$$

Then
$$n\mu d(1+\beta t) = n'\mu' d'(1+2\alpha t)$$

and
$$\beta = \frac{n'\mu' d'(1+2\alpha t) - n\mu d}{n\mu d\,.\,t}.$$

In the case of the liquid absorber, contained in a solid boat, the expansion of the liquid along the axis of the beam is determined by the coefficient of linear expansion (γ) of the boat In fact, now

$$d' = d(1+\gamma t)$$

and
$$n\mu d = \frac{n'\mu' d'(1+\alpha t)^3}{1+\gamma t}.$$
$$= n'\mu' d'(1+3\alpha t-\gamma t) \qquad \text{approximately,}$$

and
$$\beta = \frac{n'\mu' d'(1+3\alpha t-\gamma t) - n\mu d}{n\mu d\,.\,t}.$$

A Typical Experiment.

The following represents a typical set of observations carried out according to the programme oulined above :—

Metal : iron. Thickness, $d = 2{\cdot}19_4$ cm.

Intensity. Divisions per minute.

	Cold. 14° C.			Hot. 365° C.		
			Means.			Means.
Screen present	17·61	17·63		17·54	17·55	
	17·61	17·62	17·62	17·56	17·55	17·55
Screen absent	34·59	34·56		34·37	34·32	
	34·57	34·60	34·58	34·34	34·35	$34{\cdot}34_5$

Ratio of intensities:

$$R = {\cdot}5095, \qquad R' = {\cdot}5110,$$

$$X = n\mu d = {\cdot}6743, \quad X' = n'\mu' d' = {\cdot}6714.$$

X' corrected for expansion

$$= {\cdot}6714\,(1 + 2 \times 14 \times 10^{-6} \times 351)$$

$$= {\cdot}6780.$$

So
$$\beta = \frac{{\cdot}6780 - {\cdot}6743}{{\cdot}6743 \times 351} = 16 \times 10^{-6}.$$

Results.

In Table I. are set out the results of the experiments, together with deductions therefrom.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Metal.	Thickness, cm.	$R = I/E$. Expl.	Temp. °C.	$X = \log_e 1/R$.	Mean $\alpha \times 10^6$.	$X(1+2\alpha t)$.	$\beta \times 10^6$.
Lead...	$1{\cdot}33_8$	·4485	15	·8018			
		·4519	273	·7942	31	·8069	25
Iron ...	$2{\cdot}19_4$	·5092	13	·6749			
		·5112	364	·6710	14	·6776	11
		·5134	722	·6666	16	·6742	13
		·5143	1041	·6650	6	·6675	4
Tin (solid).	$2{\cdot}50_6$	·5503	15	·5974			
		·5520	200	·5942	24	·5995	19
Tin (liquid).	,,	·5385	288	·6190			
		·5413	436	·6138	38	·6228*	41
Aluminium.	$3{\cdot}19_1$	·6696	15	·4011			
		·6713	243	·3985	25	·4030	21
		·6731	513	·3959	30	·3023	35

* $X(1 + 3\alpha t - \gamma t)$ with $\gamma = 15 \times 10^{-6}$.

Column III. contains the experimental values of the ratio I/E, and represents in every case the mean of at least ten values of this quantity. In these the mean error (mean difference from mean) exceeded 1 in 1000 in only one instance (·0006 for tin at 436° C.). The resulting values of X (column V.) are of about the same reliability.

In column VI. are given the values adopted for the mean coefficient of linear expansion of the various metals over the temperature range employed. They have been deduced from the following published data :—

Lead :

0–100° : 29·3. Gruneisen, *Ann. d. Phys.* (4) xxxiii. pp. 33, 65 (1910).
0–320° : 33. Vicentini and Omodei, *Atti Tor.* xxiii. p. 38 (1887).

Iron :

0–700°. Formula in International Critical Tables, ii. p. 460.
700–1040°. { Le Chatelier, *C. R.* cxxix. p. 331 (1899).
Guillaume, Proc. Phys. Soc. xxxii. p. 374 (1920).

Tin :

18–100° : 27. Gruneisen, *Ann. d. Phys.* loc. cit.
225° : 23. Vicentini and Omodei, *loc. cit.*
20–232° : 23 to 24. Cohen and Olie, *Zeit. f. phys. Chem.* lxxi. p. 385 (1910).
226–342° : 38. Vicentini and Omodei, *loc. cit.*

Aluminium :

0–300° : 25·6 }
0–500° : 27·4 } Scheel, *Ann. d. Phys.* (4) ix. p. 837 (1902).
600° : 31·5. Le Chatelier, *C. R.* cviii. p. 1096 (1889).
0–600°. Formula in International Critical Tables, ii. p. 459.

The value ascribed to iron above 700° is of doubtful significance, as the magnitude and location of the contraction that occurs above the Curie point does not seem to be accurately known ; or, rather, it is probably considerably affected by the composition of the particular specimen. An error of as much as 40 per cent. may be involved in this particular value. The other values of α in Table I. are probably reliable to at least 5 per cent.

The values of β, the mean coefficient of atomic absorption over the range selected, are set out in column VIII. They are calculated for a selected range from the values in VII. for the upper limit of the range, and from those in V. for the lower limit. The accuracy of these results is determined chiefly by the accuracy of the experimental values of column III., and the corresponding exponentials of column V. If the two values in V., from which a result in VIII. is based, happened to be in error by half the maximum amount suggested above, and in the opposite direction, the values of β would differ from those recorded by some six units. This may reasonably be fixed as the mean limit of uncertainty in the final results as a whole. Greater accuracy than this can hardly be hoped for until the reliability of ionization methods has been increased much further than seems at present possible. This uncertainty, in the case of iron above the Curie point, might convert β into a negative coefficient; but in view of the other results, this is unlikely. With this possible exception the atomic absorption undoubtedly increases with rise of temperature.

Bearing in mind this rather large experimental error, it will be seen that the value of β in each case falls very close to the corresponding value of α in column VI. And when the whole series is considered together—dealing as it does with four different metals having widely varying values for α, and being subjected to a considerable variety of temperature conditions,—the suggestion seems highly probable that there exists an intimate connexion, if not an agreement, between the two coefficients. In other words the atomic absorption is nearly, if not exactly, a function of the linear distance between the atoms of the absorber.

Discussion.

The existence of a temperature effect on γ-ray absorption is itself somewhat unexpected; and so every care has been taken to eliminate error in the experimental work. The measurements have in some cases been repeated under a variety of conditions (as by modifying the relative dispositions of the apparatus as far as possible) without producing any appreciable change in the results. In fact, the value for lead obtained in the later experiments differs by less than the experimental error from the much less reliable results in the earlier experiments, with an entirely different absorber, furnace, electrometer, and detailed disposition of the components. This alone makes it improbable that the effect is due to any extraneous influence.

The correlation between the two coefficients here suggested is still more unexpected. Any reasonable assumption of a similar nature that might be put forward seems likely to lead to a correlation between β and the coefficient of superficial expansion (2α), since the latter might be regarded as determining the target area of the atom exposed to the radiation. The experimental accuracy is quite sufficient, however, to exclude the possibility of this correlation.

No theory seems promising at the moment; and it is thought advisable to publish the conclusions so far arrived at, as the necessity has arisen for postponing further consideration of the problem for the present. A new method of attack is under consideration, and may be carried out later.

Acknowledgments.

Much of the apparatus used in these experiments was procured through a grant from the Royal Society; while the radium was loaned by Messrs. Watson & Sons (Electro-Medical), Ltd. I have much pleasure in acknowledging my indebtedness to these two sources.

The University, Durham.
Nov. 14th, 1928.

XXXVIII. *The Duration of Contact between the Pianoforte String and a Hard Hammer.* By D. Banerji, *M.Sc.* (*Lecturer, University College of Science, Calcutta*), and R. Ganguli, *M.Sc.* (*Lecturer, Serampore College*) *.

[Plate V.]

Introduction.

In the acoustics of the pianoforte the duration of contact plays a most important part, and so its determination is of great interest.

Kaufmann's † solution of the case of the hammer striking a string of finite length at its centre is not of much practical value. In dealing with the more important case of a string struck near the end, he has assumed the shorter portion of the string to remain straight during the time of contact, and has derived an expression for the duration of contact given by the equation:

$$\frac{\tau}{\theta}=\frac{1}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}}\tan^{-1}\left[\frac{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}}{-2\frac{l}{a}+\frac{M}{m_0}}\right],$$

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* Communicated by the Authors.

† Kaufmann, Weid. *Ann.* liv. pp. 675–712 (1895).

where τ = duration of contact,
θ = period of the string,
l = total length of the string,
a = length of the shorter portion of the string,
M = mass of the string,
$m_0 = m + \rho a/3$, where m = mass of the hammer and
ρ = linear density of the string.

This equation is, however, restricted and does not hold when the shorter portion of the string is a good fraction of the total length. In a paper published in the 'Proceedings of the Royal Society,' Raman and Banerji * have therefore attempted a general solution, applicable to any point on the string. By assuming the case as similar to the problem of a loaded string, they have obtained a pressure-time equation for the struck point. Though this equation does not admit of easy analytical solution, they have nevertheless come to some very interesting conclusions, viz., that (1) the hammer gives discontinuous impulses to the string during the time of contact, and that (2) the time of contact changes discontinuously along the length of the string.

In the same paper they have also suggested another method of attacking the problem in the line of Kaufmann, which presumably has inspired Das † to extend Kaufmann's theory. On the assumption that the hammer gives discontinuous impulses at times in which the waves starting from the hammer come back to it after successive reflexions from the near end, Das has developed expressions for the pressures in successive epochs, F_1, F_2, etc., as given by the equations :

$$F_1 = 2\rho r_0 c e^{-kct},$$

$$F_2 = 2\rho r_0 c\left[e^{-kct} + e^{-k(ct-2a)}\{1 - k(ct-2a)\}\right],$$

$$F_3 = 2\rho r_0 c\left[e^{-kct} + e^{-k(ct-2a)}\{1 - k(ct-2a)\}\right.$$
$$\left. + e^{-k(ct-4a)}\left\{1 - 2k(ct-4a) + \frac{k^2}{2!}(ct-4a)^2\right\}\right], \text{ etc.,}$$

where a = distance of the striking-point from the nearer end,
ρ = linear density of the string,

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* Raman and Banerji, Proc. Roy. Soc. A, xcvii. p. 99 (1920).

† P. Das, Proc. Ind. Assoc. vii. pts. 1 & 2, pp. 13-20 (1921).

v_0 = initial velocity of the hammer,
c = velocity of propagation of transverse waves on the string,
$k = 2\rho/m$, where m = mass of the hammer,
t = variable time.

Das's solution is also of limited applicability, but it is worth while to see how much it can claim to be an advance on Kaufmann's. It may be noted in the meantime that the determination of duration of contact from Das's equations involves long and tedious calculations and laborious graphical methods.

The earliest experimental work on the pianoforte was made by Hipkins[*] and next by Kaufmann[†]. Observations on the nature in which the duration of contact changes with the struck point appear to have first been taken by Raman and Banerji[‡] by an electrical method. George[§] remarks that this method is open to objection, but he has never attempted to verify directly the conclusions arrived at by Raman and Banerji, neither has there been any attempt to test Das's pressure-time equations. All that George or R. N. Ghosh[||] has done generally concerns Kaufmann's theory. Das[¶] has, however, in a later paper tried to show that his theory is indirectly supported by the results of an investigation on the energy of struck strings carried out by George and Backett[**]. But, very recently, Kar, Ganguli, and Laha[††] found Das's theory to have no agreement with experimental evidence regarding the amplitudes of the different harmonics of struck strings. Furthermore, a careful study on the duration of contact—the most important element in the acoustics of struck strings—seems still to be wanting.

In the present paper attempts have been made to (1) determine accurately the duration of contact between the hammer and string when the latter is struck at various points along its length, and the manner in which this duration changes with the struck point ; to (2) compare the experimental values with those calculated respectively from Das and Kaufmann's theories ; and further to (3) study the condition of the shorter portion of the string during the time of contact.

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[*] Hipkins, Proc. Roy. Soc. A, xxxvii. pp. 37–39, and xxxviii. p. 83 (1884).

[†] Kaufmann, *loc. cit.*

[‡] Raman and Banerji, *loc. cit.*

[§] George, Phil. Mag. xlvii. pp. 34 & 48 (1924), pp. 91–99 (1924); Proc. Roy. Soc. A, cviii. pp. 284–295 (1925).

[||] R. N. Ghosh, Phil. Mag. xlvii. p. 125 (1925); Proc. Ind. Assoc. ix. pp. 111 & 194 (1925); Phys. Rev. xxiv. p. 456 (1924), xxxvii. p. 135 (1926).

[¶] Das, Ind. Journ. Phys. i. p. 437.

[**] George and Beckett, Proc. Roy. Soc. A, cxiv. (1927).

[††] Kar, Ganguli, and Laha, Phil. Mag., March 1928.

Experiment.

A string 240 cm. long and of mass 16·4 gm. was employed. One of its ends was tied to a firm support rigidly fixed on a table, and the other end, passing over an equally rigid fixed pulley, carried a heavy weight. Two vertical rafters, attached one to each end of the table, carried a horizontal rod at the top, from which a ball was freely suspended by fine threads, so that it just touched the string while at rest. This ball constituted the striking-hammer. The struck point was illuminated from above by an arc-lamp and focussed by a lens on a long and shallow wooden camera, with a slit in the middle of the cover and placed along the base of the table. The slide was pulled with a uniform high velocity from one end of the camera to its other end by a motor. The start of the motor was made simultaneous with the release of the striking-hammer by means of an electromagnetic arrangement. The cover of the slide was automatically closed on reaching the other end of the camera, and timing was so adjusted that the hammer impinged on the string just when the slide was carried across the slit.

Figs. 9 to 11 (Pl. V.) are specimen photographs of the time-displacement pictures that were obtained. Fig. 9 was obtained with a hammer of mass 46 gm. striking at 32 cm. from the end, and figs. 10 and 11 were obtained with a hammer of mass 13·4 gm. for 35 and 40 cm. respectively.

The speed of the motor could be regulated as desired. With a certain convenient speed the wave-form of the string vibrating under the tension of 10,903 kilograms was photographed. The distance from one crest to the next of the wave-picture is the distance traversed by the slide within the known period of the string. The velocity of the slide being thus accurately measured, the duration of contact was calculated from the time-displacement picture of the struck point by measurement along the time-axis of the distance intercepted between the point of first contact and the point where it left the string.

Results and Discussion.

In the time-displacement picture of the struck point it is not always possible to find exactly where the hammer leaves the string. In such cases, however, the vibration period of the shorter portion of the string is small compared with the duration of contact, and the correction to be applied for uncertainties in the measurement of the duration of contact is minimized by a comparison between the time-displacement picture of the struck point and that of a point on the shorter portion of the string very near to the struck point.

The duration of contact for different struck points in the case of a striking-hammer of mass 46 gm. is given in Table I. and graphically shown in fig. 1. Table II. gives the case of a striking-hammer of mass 13·4 gm. A comparison between experimental values and those calculated respectively from Das and Kaufmann's theories is given therein and graphically shown in fig. 2. The experimental curve is found to be not quite smooth like the curve of Kaufmann, but is kinked. From fig. 2 it appears that the mean slope of the experimental curve (neglecting the kinks) changes in a manner similar to that of Das's. The kinks in our experimental curve owing to the discontinuous change are, however, far less prominent than those obtained in the theoretical curve of Das. Though the slope of the curve changes somewhat abruptly near the kinks, it never changes sign as predicted by Das. The table

TABLE I.

$\frac{M}{m} = 0{\cdot}3565.$ $\theta = 0{\cdot}0356$ sec.

Velocity of the plate = 76·33 cm./sec.

a (cm.).	τ (sec.).
15	·0262
20	·0263
25	·0356
32	·0369
40	·0432
50	·0432
60	·0445
80	·0511
100	·0590

Fig. 1.

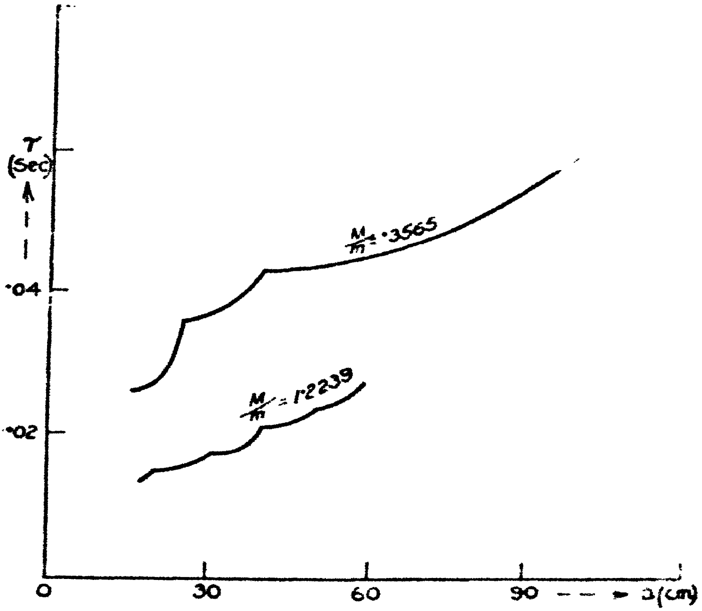


TABLE II.

$\frac{M}{m} = 1 \cdot 2239.$ $v_0 = 51 \cdot 39$ cm./sec.

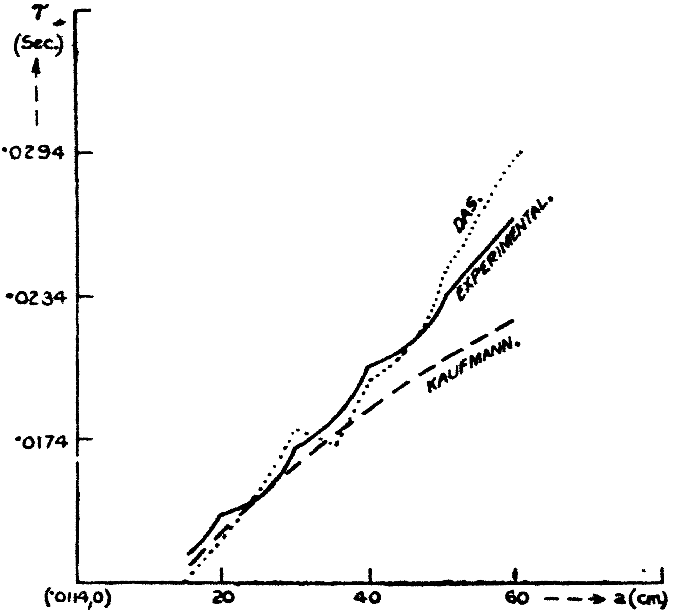
$\theta = 0 \cdot 0356$ sec. $\rho = 0 \cdot 0569$ gm.

	τ (sec.).		
	Experimental.	From Das's theory.	From Kaufmann's theory.
15	·0123	·0114	·0117
20	·0142	·0131	·0113
25	·0151	·0153	·0150
30	·0170	·0179	·0164
35	·0179	·0173	·0176
40	·0205	·0198	·0189
45	·0211	·0210	·0200
50	·0233	·0241	·0209
55	·0248	·0268	·0217
60	·0266	·0292	·0223

shows clearly enough how much on the whole Das's theory can claim to be an advance on Kaufmann's.

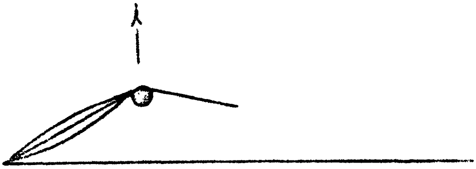
Figs. 4 to 8 (Pl. V.) give the vibration pictures of the shorter portion of the string under different conditions. Only Kaufmann obtained similar pictures, but it is curious that he did not take much notice of them, apparently on the ground that his string was thin and hammer massive. The figures in the present paper, however, clearly show that the shorter portion of the string starts vibrating at the instant the hammer impinges on the string, and continues to vibrate quite independently during the time of contact with nodes—one at the struck point and the other at the fixed end—and a loop at the middle, just as a string of the same length would vibrate under the same tension. It further shows that this vibratory character is maintained even for $\frac{M}{m} = 1{\cdot}2239$, and that its mean position at any instant is similar to that of a straight rod as contemplated by Kaufmann. Fig. 7 is the vibration picture of the middle point of the shorter portion of the string, and figs. 6 and 8 are those of points close to the struck point and the end respectively. It will be found that the displacement of any

Fig. 2.



of the above points is fairly proportional to its distance from the end. For illustration of the condition of the shorter portion of the string at any instant see fig. 3. Figs. 4 and 5 (Pl. V.) are vibration pictures of points 17 and 25 cm. respectively from the end for $m = 46$ gm., striking at 25 and 32 cm. respectively from the end. A proportional change in the period is clearly noticeable. After the separation of the hammer from the string, the whole string vibrates in a manner which appears to be largely dependent on the period of the shorter portion of the string.

Fig. 3.



Vibration pictures of the other side of the string have also been taken, but are not reproduced here. They will be the subject matter of a later communication.

Conclusions.

1. The curve showing the relation between the distance of the struck point and the duration of contact of the hammer with the string is not smooth like the theoretical curve of Kaufmann, but appears to be kinked. The mean slope of the kinked experimental curve agrees somewhat better with Das's theoretical curve. The actual kinks are, however, far less marked than those obtained in the theoretical curve due to the discontinuous changes predicted by Das. Though the slope of the curve changes somewhat abruptly near the kinks, it never changes sign as in Das's theoretical curve.
2. During the time of contact, while the struck point follows the movement of the hammer, the shorter portion of the string instead of remaining straight as contemplated by Kaufmann executes its fundamental mode of vibration.

Further work in this line is in progress and will form the subject of a future communication.

In conclusion we express our best thanks to Prof. S. K. Mitra for his interest in the work.

University College of Science,
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June 21, 1928.

XXXIX. *The Absorption of X-Rays from* 0·63 *to* 2 *Å.U.* *By* IVOR BACKHURST, *M.Sc., Physics Department, National Physical Laboratory* *.

Introduction.

MOST recorded measurements of monochromatic X-ray absorption have been for wave-lengths less than 1·0 Å.U., but the exact manner in which the true or fluorescent absorption depends on wave-length is to some extent obscured for most elements at short wave-lengths by the appreciable and uncertain relative magnitude of the scattering effect. The measurements of which an account is given here have been made for wave-lengths between 0·63 and 2 Å.U., for which the relation between absorption and wave-length may be obtained free from such uncertainty, the scattering being negligible. Included in this region of wave-length are the L discontinuities of platinum and gold, the K discontinuity of copper, and a possible multiple ionization discontinuity of silver. Departures from the cube law of absorption have been found that are sufficiently well marked to be well beyond suspicion of coming within the margin of experimental error. It is desired to emphasize this point, as well-known writers (1) have from time to time expressed the opinion that no real departure from the cube law had been definitely established. Direct methods of measurement have been used throughout to determine the absolute value of the mass absorption coefficient; balance methods furnishing the absorption relative to aluminium have been used as well, but only to provide check measurements.

The principal difficulty in the direct measurement of absorption, as frequently mentioned in the literature of the subject, is the maintenance of constant X-ray intensity, involving as it does the constancy of both potential and current of the X-ray tube, and the constancy of position of focal spot and similar factors. This difficulty is greater for longer than for shorter wave-lengths, as larger currents are needed in the former case to compensate for the lower potential and consequent reduction in intensity. Special care was on this account taken in the arrangement and design of the apparatus to secure a constant and intense X-ray beam, and the experimental arrangement will therefore be described in some detail. It is thought that the principal error in the present research has probably occurred in the measurement of the effective mass per unit area of the very thin sheets of absorbing material, as with an X-ray beam of necessarily small cross-sectional area the mass of absorbing element in its path was always very small, and often less than 0·05 milligramme. This error was, however, reduced as far as possible by the use of a number of sheets, and results obtained with different sheets rarely differed by more than 2 per cent.

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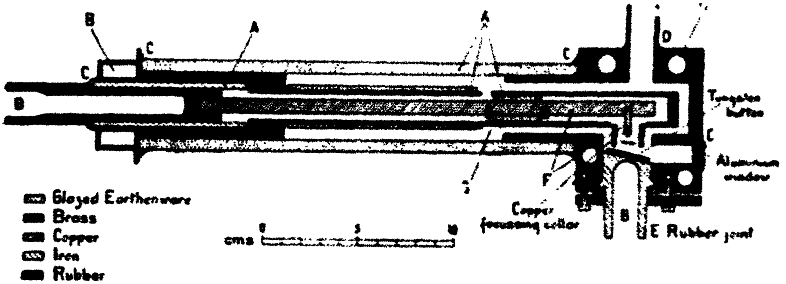
* Communicated by Dr. G. W. C. Kaye.

Apparatus and Method of Experiment.

The X-ray tube, of which a horizontal section is shown to scale in fig. 1, had a tungsten filament cathode and was a modification of one described by Siegbahn. It was designed to utilize the full power of the high-tension supply over the voltage range required and to allow easy changing of the anticathode. The insulating tubes A were of glazed earthenware and were unpuncturable at the voltages used. The anticathode end of the X-ray tube was made by drilling a rectangular brass block. This method of construction avoided the use of soldered joints in any position where a leak would introduce vapour from the water-cooling system and be troublesome to locate. Both upper and lower faces of the brass block were water-cooled, and water-channels B were drilled through the block. The tungsten anticathode consisted of a tungsten button welded to an iron base which was water-cooled. Copper and iron anticathodes were also used. This end of the X-ray tube was earth connected and vigorously cooled from the main supply; the other end was at high potential and cooled from a thermo-syphon. The vacuum joints were the four wax joints C, the soldered one D, and the rubber one E. The latter was held by a

Fig. 1.



clamping ring with steel screws, removal of which enabled the anticathode to be changed, the tungsten filament renewed, or the focussing collar adjusted. The window was aluminium foil. The rods F were copper, the remaining parts of the X-ray tube not mentioned above were brass. The vacuum was maintained by two mercury-diffusion pumps in series supported by a rotary oil pump, and ice traps prevented condensation of mercury in the X-ray tube. Liquid air or other mercury-vapour traps were found unnecessary, as a tungsten filament would last for several months if not placed too near the axis of the focussing collar, and the tube would not pass a measurable current unless the filament was heated. The glazed earthenware tube immediately surrounding the brass tube G prevented the latter from sputtering on to the main insulating tube, as it otherwise would have done in the presence of mercury vapour. Periodical dismantling was thereby avoided, and it was unnecessary to undo any joint except the rubber one.

The tube current ranged from 35 milliamps. at 25 kilovolts to 80 milliamps. at 11 kilovolts, and a sufficiently strong X-ray beam was furnished to enable the general radiation to be used as well as the characteristic. This facilitated the close investigation of certain regions of wave-length such as those of the L-absorption edges. The general radiation, even with a tungsten anticathode, was weaker than the characteristic under the conditions of experiment, but it was particularly desirable with the general radiation to employ a small angular width of reflected beam in order that the latter might be nearly enough homogeneous. It was consequently very important that the intensity of the primary beam should be as high as possible.

The high-tension supply was not a constant potential one, but a satisfactory constant effective potential was obtained by supplying a high-tension transformer with current from a rotary converter driven by a battery. The transformer was of the "power" type, with ample iron core, and rheostats were excluded from the supply circuit, so that the voltage applied to the X-ray tube was inappreciably affected by small fluctuations in tube current. Alteration of voltage was effected by means of an auto-transformer and by connecting in series or parallel the two windings of the high-tension transformer. The filament temperature and the focussing collar determined the amount of the tube current, and slight variations in the latter during an experiment were corrected by means of a rheostat controlling the filament current. This was supplied from a battery, and the tube current could be maintained constant to within 1 per cent. It was found possible to adjust the focussing collar so that an increase of tube current above a chosen value C made comparatively little difference to the intensity of the X-ray beam. By making the value of C somewhat less than the amount of current available the tube could be operated at a maximum current, while small variations in the latter produced little effect on X-ray intensity. The distance between the focussing collar containing the tungsten filament and the anticathode being very short (between 3 and 6 mm. along the axis), there was little movement of focal spot, and the primary X-ray beam made an angle of about 10° with the face of the anticathode.

In consequence of the above arrangements, the steadiness of the beam obtained after reflexion from a calcite crystal was quite satisfactory, and errors produced by fluctuations in X-ray intensity were less than those introduced in the observation of electrometer deflexions. About 1 per cent. fluctuation occurred amongst individual readings of these, but the mean of at least five readings was invariably taken.

As one slit was included in the window of the X-ray tube, only one lead slit was required on the spectrometer between the tube and the crystal. The reflected beam passed through two lead slits A and B before entering the ionization chamber, one of the slits B being close to the latter. The absorbing screen was held by a spring clamp flat against the face of slit A on the side next the crystal. The maximum angular width of the reflected beam passing into the ionization chamber was determined by slits A and B, and varied from 4·5′ of arc for the shorter wave-lengths to 45′ for the longer. The corresponding range of wave-length included in the width of the beam was therefore between 4 and 6 per cent. Narrower slits were used for characteristic radiation, although this width was necessary to obtain satisfactory intensity with general radiation; but it will be shown that negligible error was thereby occasioned.

At potentials between 10 and 25 kilovolts, as was found by Wagner and Kulenkampff(2), the wave-length ($\lambda_m/2$) is somewhat shorter than the shortest wave-length excited by the voltage on the tube, if λ_m is the wave-length of maximum intensity of the general radiation, intensity being measured by the ionization method. In the present investigation the tube voltage was always adjusted to a value somewhat less than that required to excite $\lambda/2$, where λ was the wave-length selected by the crystal, so that λ was always nearly equal to λ_m, and the rate of variation of intensity with λ was practically zero over the width of the beam. Under these conditions we have for the experimental value "μ_a" of the absorption coefficient "μ" at a wave-length $\lambda_a=(\lambda_1+\lambda_2)/2$,

$$\mu_a = (1/t)\log\left[(\lambda_2-\lambda_1)\Big/\int_{\lambda_1}^{\lambda_2} e^{-\mu t}\,d\lambda\right], \quad \text{where } I=I_0e^{-\mu t}.$$

The thickness "t" of the absorbing screen was chosen so that the wave-length investigated was in the neighbourhood of the value "λ_0" for which $\mu t=(n-1)/n$, where $\mu=k\lambda^n$, k being constant. This is a point of inflexion on the curve $I=f(\lambda)$, which is very nearly a straight line in this region if n is approximately 3. A sufficient number of absorbing screens were used to keep the ratio I_0/I between the limits 1·8 and 2·5, so that the errors due to inhomogeneity of beam were as follows:—

For the case $n=3$, the first limit corresponds to

$$\lambda_1 = 0{\cdot}93\,\lambda_0, \qquad \lambda_2 = 0{\cdot}99\,\lambda_0$$

for the maximum width of beam, and the difference between the experimental value μ_a and the true value $k\lambda_a^n$ is less than 0·08 per cent., while for the second limit

$$\lambda_1 = 1{\cdot}09\,\lambda_0, \qquad \lambda_2 = 1{\cdot}15\,\lambda_0,$$

and $k\lambda_a^n-\mu_a$ is less than 0·3 per cent. For intermediate values of I_0/I the error is less and travels through a zero value. The upper limit of I_0/I was taken further from the value, for which $\mu t=(n-1)/n$, than the lower limit, on account of the fact that the percentage error in the value found for μ is $(1/\mu t)\times$ percentage error in I_0/I, so that it was desirable to have μt not much less than unity.

Two crystals and two ionization chambers were mounted on the spectrometer, so that the balance method could be used to check values found with a single chamber by the direct method. The latter was the method mostly used as it afforded greater sensitivity. The ionization current was measured with a Compton electrometer, the time for a given deflexion (approximately the last two-thirds of the deflexion from zero) being observed with and without the absorbing screen in position. The rate of deflexion over the observed range was very nearly constant, and the correction for "natural leak" varied from ½ to 1 per cent. Sulphur insulation was used throughout. The ionization chambers were filled with methyl bromide.

The slit B, close to an ionization chamber, subtended at no point in the absorbing screen a solid angle greater than

0·00003 of a complete solid angle, so that the fraction entering the ionization chamber of the total scattered radiation from the absorbing screen was quite inappreciable. With the ionization chamber set just out of position for reception of the reflected beam, no ionization current could be observed, the amount of scattered radiation from other sources being therefore also negligible. This was further checked by exposure for several hours of a photographic film between the slits A and B, with the ionization chamber set to receive the reflected beam.

In the case of aluminium, the absorbing screens were made from rolled sheets of the metal, but the screens of other elements were built up from carefully-selected sheets of beaten leaf. The mass per unit area was found by weighing, so that determination of the mass absorption coefficient "μ/ρ" did not involve a knowledge of the density ρ. In measuring the absorption, the screen was moved for each observation in such a manner that the narrow strip areas effecting the absorption were approximately evenly spaced over the weighed area. At least ten readings were included in a set and were taken alternately with and without the absorption screen in position. Usually not more than 3 per cent. difference existed between the greatest and least values found for the absorption coefficient, when the latter was calculated separately from each of the five pairs of readings. This was considered to indicate a reasonable degree of uniformity in the thickness of the screens, in view of the fact that the total thickness mostly lay between 0·001 and 0·01 mm. All the screens were made from metal of a high degree of purity.

Results.

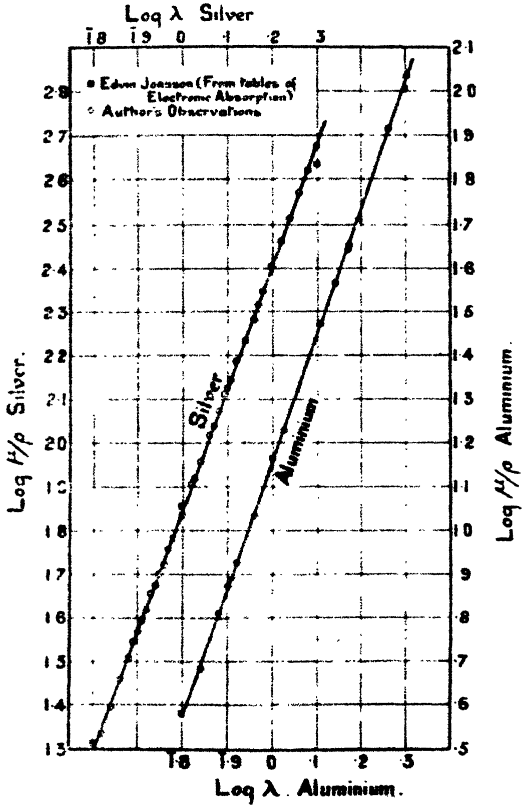
Since the mass-scattering coefficient σ/ρ is not known at all accurately, and is in these experiments only a very small fraction of μ/ρ, the results are given in terms of the latter rather than of the mass fluorescent absorption coefficient τ/ρ, which is obtained from μ/ρ by subtracting σ/ρ. With the logarithm of μ/ρ plotted against the logarithm of the wave-length λ, the experimental points were found to lie on straight lines within the limits of observational error, but with μ/ρ plotted against λ^3 straight lines within the limits of error were not generally obtained. The results are therefore best represented by equations of the form $\mu/\rho=a\lambda^n$. In the graphical representation $\log \mu/\rho$ has been plotted against $\log \lambda$ rather than μ/ρ against λ^n, as in the former method circles having the same radii and drawn with the experimental points as centres can be used to denote the same percentage error in μ/ρ and λ for all points of the graph.

Silver.

For silver, using the method of least squares and a log graph (fig. 2), the equation calculated is

$$\log \mu/\rho = 1{\cdot}844 + 2{\cdot}79 \log \lambda, \quad \text{or} \quad \mu/\rho = 69{\cdot}9\,\lambda^{2{\cdot}79}. \qquad (1)$$

Fig. 2.



The experimental points are given in Table I.; circles with 1 per cent. radii drawn on them on the log graph are all cut by the straight line represented by (1). On a $(\mu/\rho, \lambda^3)$ graph, equation (1) represents an appreciably curved line. The straight line approximating to it with the condition that the maximum percentage difference in μ/ρ should be less than for any other has the equation

$$\mu/\rho = 62\cdot4\lambda^3 + 4\cdot47. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Its maximum difference is 4·25 per cent., well beyond the limits of experimental error, and the term 4·47 is too high to represent σ/ρ. The experimental data cannot therefore be expressed properly by one equation of the form

$$\mu/\rho = a\lambda^3 + b.$$

Alexander[(3)] has suggested that in the neighbourhood of $\lambda = 1\cdot0$ Å.U. there is a break in the absorption curve, and that two equations,

$$\mu/\rho = a\lambda^3 + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

and

$$\mu/\rho = a'\lambda^3 + b', \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

TABLE I.

	Log μ/ρ.			Log μ/ρ.	
Log λ.	Silver.	Gold.	Log λ.	Silver.	Gold.
$\bar{1}$·82	1·335	1·969	0·024	—	1·909
$\bar{1}$·84	1·395	2·024	0·027	1·920	—
$\bar{1}$·86	1·459	2·087	0·04	1·958	1·956
$\bar{1}$·88	1·510	2·140	0·06	2·018	2·009
$\bar{1}$·89	1·545	—	0·07	2·038	2·031
$\bar{1}$·90	1·568	2·202	0·08	2·072	2·062
$\bar{1}$·91	1·594	—	0·094	2·112	—
$\bar{1}$·92	1·620	—	0·10	2·126	2·104
$\bar{1}$·928	—	2·265	0·107	2·145	—
$\bar{1}$·93	1·656	—	0·12	2·186	2·168
$\bar{1}$·94	1·672	2·219	0·14	2·234	2·217
$\bar{1}$·948	—	2·245	0·16	2·283	2·267
$\bar{1}$·95	1·702	—	0·17	2·315	2·291
$\bar{1}$·96	1·723	2·159	0·18	2·348	2·319
$\bar{1}$·97	1·757	2·168	0·20	2·403	2·372
$\bar{1}$·98	1·784	2·198	0·22	2·460	2·423
$\bar{1}$·99	—	2·225	0·24	2·513	2·469
0·00	1·835	2·252	0·26	2·572	2·528
0·01	—	2·267	0·28	2·623	2·577
0·02	1·906	—	0·30	2·679	2·630

will accurately represent the data in this region of wavelength. If the values in Table I. are plotted on a $(\mu/\rho, \lambda^3)$ graph, it at once appears that two straight lines will provide a good fit, but it is difficult to select the exact point for the break, as the eye is influenced by the spacing of the points, and is apt to make insufficient allowance for the disparity in the percentage errors represented by equal distances at different parts of the graph. A change of scale of the graph may produce a change in the apparent position of the break. It seems as well, therefore, to use some method of fixing the latter other than simple inspection of the graph, and a method that appears to be as good as any is to assume that equation (1) is accurate and determine equations (3) and (4) so that the maximum percentage difference between corresponding values of μ/ρ calculated from (1) and from (3) and (4) should be less than for any other pair of equations similar to (3) and (4). This particular condition is chosen since the experimental error is approximately a constant percentage of μ/ρ, while the value of μ/ρ varies from 20 to 500. The position found for the break in this way is at $\sqrt{\lambda_1\lambda_2}$, where λ_1 and λ_2 are the limits of the wavelength range over which the approximation is made. This follows from the fact that, if $\mu/\rho = k\lambda^n$ is approximated to with the above condition by one equation $\mu/\rho = a\lambda^3 + b$, the maximum percentage error E in μ/ρ is dependent only on n and λ_1/λ_2, being given by

$$\mathrm{E} = \frac{100\,\mathrm{N}}{2+\mathrm{N}},$$

where

$$\mathrm{N} = m^m\left(\frac{1-p}{1-p^m}\right)\left\{\frac{\frac{1-p}{1-p^m}-1}{1-m}\right\}^{m-1} - 1,$$

and

$$m = n/3, \quad p = \lambda_1^3/\lambda_2^3, \quad m<1, \quad \text{and} \quad p<1.$$

The further p departs from unity the greater the value of E, so that with two equations of the form $\mu/\rho = a\lambda^3 + b$, for the minimum value of E, $\lambda_1/\lambda_B = \lambda_B/\lambda_3$ or $\sqrt{\lambda_1\lambda_2} = \lambda_B$, the wavelength of the break.

In this way the position of the break in the L-absorption curve for silver is fixed at 1·122 A.U., and the two equations are

$$\mu/\rho = 67{\cdot}0\,\lambda^3 + 2{\cdot}71 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\mu/\rho = 59{\cdot}4\,\lambda^3 + 13{\cdot}5, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the maximum percentage difference in μ/ρ between (1) and (3) (4) calculated on μ/ρ from (1) being less than 1·2. Using Allen's⁽⁴⁾ results, Alexander has given the equations

$$\mu/\rho = 74{\cdot}1\,\lambda^3 + 2{\cdot}0 \quad \text{and} \quad \mu/\rho = 55{\cdot}8\,\lambda^3 + 27{\cdot}0,$$

which put the break at 1·110 Å.U. Allen represented his experimental data by two equations of the form

$$\mu/\rho = a\lambda^n + \sigma/\rho,$$

and found 1·10 Å.U. as the wave-length at which there occurred a change in the index n from 2·92 to 2·6, the constant "a" changing from 73 to 76 or 78, and the true mass-scattering coefficient σ/ρ being regarded as negligible.

It seems very questionable as to what extent any special physical significance should be attached to such a break, in the absence of other than absorption data, since it is also possible to represent μ/ρ by a continuous function of λ. Alexander has deduced a theory of multiple ionization from the possible positions of breaks in K-absorption curves, and found that $\lambda_{KK'}$, the wave-length of a break, was inversely proportional to A^2, A being atomic number. It should be noted, however, that a law something of this nature seems to be a necessary consequence of considerations such as the following. The data upon which the law depends are thirteen values of $\lambda_{KK'}$, six of which are for elements Fe, Ni, Cu, and Zn (A from 26 to 30), and on a graph of $\sqrt{1/\lambda}$ against A are clustered in a group and serve only to fix rather approximately one point of the curve. Two values, *i. e.* for Mo and Ag, are based on Richtmyer's⁽⁵⁾ results; but the remaining five, which are deduced from Allen's results for Ag, Sn, W, Pt, and Au (A from 47 to 79), mainly determine the nature of the curve. For these five elements Allen found that $\mu/\rho = a\lambda^n + \sigma/\rho$, in each case n having the same value, 2·92, and the data extending from 0·08 Å.U. to λ_K, the wave-length of the K-absorption edge. If the data for each element are represented by two equations of the form $\mu/\rho = a\lambda^3 + b$, with the condition that for any value of λ the maximum percentage difference in the values of μ/ρ, calculated from the appropriate one of these equations and from Allen's equation, should be less than for any other pair of equations of the form $\mu/\rho = a\lambda^3 + b$, then, as shown above, it follows that

$$\lambda_{KK'} = \sqrt{\lambda_1\lambda_2} = \sqrt{0{\cdot}08\,\lambda_K}$$

for each element. Since λ_K is inversely proportional to A^2, the law, $\lambda_{KK'}$ inversely proportional to A, is a necessary consequence, and would give a somewhat better fit to the data than the law, λ_{KK} inversely proportional to A^2, deduced by Alexander. It may further be remarked that, while in the case of these elements two equations of the form $\mu/\rho=a\lambda^3+b$ are being used to approximate to an equation of the form $\mu/\rho=c\lambda^{2\cdot92}+d$ between limits of wave-length $\lambda_1=0\cdot08$ Å.U. and $\lambda_2=0\cdot153$ Å.U. to 0·485 Å.U., only one equation of the form $\mu/\rho=a\lambda^3+b$ is used for Al, for which the same index $n=2\cdot92$ was found by Allen to hold over a range $\lambda_1=0\cdot08$ Å.U. to $\lambda_2=2$ Å.U. Yet, as shown above, the degree of approximation depends only on n and λ_1/λ_2, so that in the case of each of the elements Ag, Sn, W, Pt and Au, the data could be better represented by one equation of the form $\mu/\rho=a\lambda^3+b$, with no break at all, than could the data for Al, for which one equation is made to serve since no multiple ionization effect would be expected for Al in this region of wave-length.

On the whole it would appear that, as far as the experimental results go, there is nothing to indicate discontinuities of a type attributable to multiple ionization phenomena. On the theoretical side it is not at all clear why multiple ionization should be expected to produce discontinuities of the above type. This question has been investigated by Richtmyer (6), who, with the help of recent data, has extended Turner's (7) calculation of the energy necessary for double K ionization on the basis of Wentzel's (8) theory, and finds that for elements of atomic number up to 51 it should be greater than twice that required for single ionization. The wave-lengths of the breaks considered above correspond to considerably smaller energy values. On account of this and other reasons, Richtmyer deduces that there is no theoretical justification for the conclusion that any obvious relation should exist between such discontinuities and multiple ionization. Recently Edvin Jonsson (9) has obtained results which show that when allowance is made for the K, L, M, etc. absorption jumps, the average electronic absorption μ_e is for all elements the same function of Nλ, or very nearly so, N being atomic number. The function of Nλ is such that for any element the absorption curve on a ($\log\mu/\rho$, $\log\lambda$) graph is quite continuous apart from the K, L, M, etc. absorption jumps. Values taken from Jonsson's tables are plotted in fig. 2, and show quite good agreement, except between 1·5 and 2 Å.U.

Aluminium.

Experimental values for aluminium are shown in Table II.,

TABLE II.

	Log μ/ρ.			Log μ/ρ.	
Log λ.	Aluminium.	Copper.	Log λ.	Aluminium.	Copper.
$\bar{1}$·84	0·685	1·680	0·12	—	2·440
$\bar{1}$·88	0·811	1·791	0·141	1·568	—
$\bar{1}$·90	0·875	—	0·17	1·642	1·670
$\bar{1}$·91	0·896	—	0·172	1·651	—
$\bar{1}$·92	0·928	1·900	0·186	—	1·726
$\bar{1}$·96	1·035	2·000	0·195	1·711	—
0·00	—	2·128	0·24	—	1·865
0·027	1·230	2·179	0·26	1·920	1·946
0·04	—	2·230	0·28	—	1·997
0·107	1·472	2·416	0·30	2·040	2·064

and applying the method of least squares to obtain the best straight line on a log graph (fig. 2), the equation found is

$$\log \mu/\rho = 1\cdot156 + 2\cdot91 \log \lambda \quad \text{or} \quad \mu/\rho = 14\cdot3\,\lambda^{2\cdot91}. \qquad (7)$$

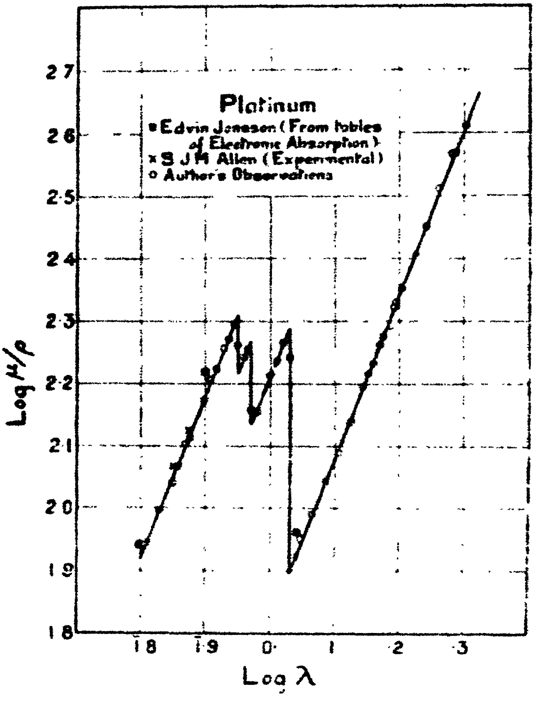
This straight line cuts every circle drawn with an experimental point as centre and radius representing 1 per cent. The curve that equation (7) represents on a $(\mu/\rho, \lambda^3)$ graph can, however, be closely approximated to by a straight line. The maximum percentage difference between corresponding values of μ/ρ calculated from (7) and from

$$\mu/\rho = 13\cdot67\,\lambda^3 + 0\cdot388 \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

for any value of λ between the limits $\log \lambda = \bar{1}\cdot8$ and $\log \lambda = 0\cdot3$ is 1·9, and is less than for any other straight line on the $(\mu/\rho, \lambda^3)$ graph, percentage being reckoned on the value of μ/ρ from (7). If on this graph an ellipse is drawn, with each experimental point as centre, having semiaxes representing 1 per cent. change in μ/ρ and λ respectively, the straight line (8) will just cut most of these ellipses, but the fit is certainly not so good as with (7). The value 0·388 so obtained for σ/ρ, although the latter is not known at all accurately, must certainly be too high, but the agreement between (7) and (8) becomes appreciably poorer if a value as low as, say, 0·15 is put for the constant term of (8).

Allen's equation $\tau/\rho = 14{\cdot}0\,\lambda^{2{\cdot}92}$ is in good agreement with (7). Martin (10) found $\mu/\rho = 13{\cdot}9\,\lambda^{2{\cdot}98}$, but considered that the cube law also represented his results within experimental error. Values from Jonsson's table (fig. 2) are in good agreement with (7), but show an index rather less than 2·91 between 1 and 2 A.U. On the whole it would appear fairly certain that the fluorescent absorption in aluminium between 0·5 and 2·0 A.U. is very nearly proportional to λ^3, but not accurately so, the value of the index being definitely somewhat less than three.

Fig. 3.



Platinum and Gold.

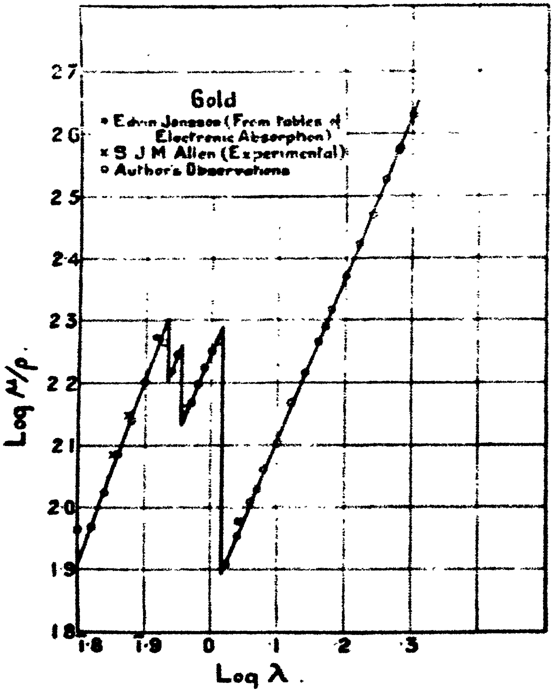
For platinum and gold the region of wave-length around the L-absorption edges was investigated closely with the object of measuring the magnitudes of the L-absorption jumps as accurately as possible. As shown in fig. 3 and Table III. for platinum, and fig. 4 and Table I. for gold, the values of log μ/ρ plotted against log λ were in each case

TABLE III.

Platinum.

Log λ.	Log μ/ρ.	Log λ.	Log μ/ρ.	Log λ.	Log μ/ρ.
$\bar{1}$·809	1·946	1·965	2·255	0·1516	2·216
$\bar{1}$·829	1·997	$\bar{1}$·97	2·159	0·16	2·232
$\bar{1}$·849	2·041	$\bar{1}$·98	2·156	0·17	2·263
$\bar{1}$·859	2·068	0·00	2·214	0·175	2·277
$\bar{1}$·869	2·104	0·01	2·237	0·187	2·293
1·877	2·115	0·02	2·266	0·191	2·322
$\bar{1}$·899	2·173	0·03	2·242	0·195	2·331
$\bar{1}$·909	2·206	0·04	1·923	0·204	2·354
$\bar{1}$·918	2·223	0·047	1·952	0·224	2·407
$\bar{1}$·929	2·257	0·065	1·992	0·24	2·452
1·937	2·272	0·086	2·044	0·26	2·512
1·947	2·296	0·106	2·091	0·28	2·568
1·950	2·262	0·124	2·140	0·30	2·610
$\bar{1}$·96	2·242	0·143	2·196	—	—

Fig. 4.



found to fall on four straight lines within the limits of experimental error. The equations for platinum are:

$$\log \mu/\rho = 2{\cdot}443 + 2{\cdot}60 \log \lambda, \quad . \quad . \quad . \quad (9)$$

$$\log \mu/\rho = 2{\cdot}347 + 2{\cdot}60 \log \lambda, \quad . \quad . \quad . \quad (10)$$

$$\log \mu/\rho = 2{\cdot}210 + 2{\cdot}60 \log \lambda, \quad . \quad . \quad . \quad (11)$$

$$\log \mu/\rho = 1{\cdot}816 + 2{\cdot}64 \log \lambda\,; \quad . \quad . \quad . \quad (12)$$

and for gold:

$$\log \mu/\rho = 2{\cdot}495 + 2{\cdot}91 \log \lambda, \quad . \quad . \quad . \quad (13)$$

$$\log \mu/\rho = 2{\cdot}395 + 2{\cdot}91 \log \lambda, \quad . \quad . \quad . \quad (14)$$

$$\log \mu/\rho = 2{\cdot}251 + 2{\cdot}64 \log \lambda, \quad . \quad . \quad . \quad (15)$$

$$\log \mu/\rho = 1{\cdot}848 + 2{\cdot}61 \log \lambda. \quad . \quad . \quad , \quad (16)$$

If $\log \mu/\rho$ at the absorption edge L_1 (the edge having the shortest wave-length of L_1, L_2, L_3) is calculated from each of these equations and differences are taken, the values given in column S of Table IV. are obtained.

TABLE IV.

	Levels compared.	R= Log of ratio of energy levels.	S= Log of ratio of absorption coefficients.	R−S.
Platinum.	L_1/M_1	0·625	0·629	−0·004
	L_2/M_1	0·604	0·533	0·071
	L_3/M_1	0·544	0·396	0·148
Gold	L_1/M_1	0·623	0·628	−0·005
	L_2/M_1	0·603	0·528	0·075
	L_3/M_1	0·541	0·401	0·140

It has been found by E. Jonsson that the total L-absorption jump is equal to the ratio of the energy levels L_1 and M_1, and the figures in Table IV. agree with this to about 1 per cent. The same rule evidently does not hold for the partial L jumps, but in the case of platinum and gold the following equalities may be noted:

$$J(L_1/M_1) = (E_{L_1}/E_{M_1}), \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$J(L_2/M_1) = \frac{1}{k}(E_{L_2}/E_{M_1}), \quad . \quad . \quad . \quad . \quad (18)$$

$$J(L_3/M_1) = \frac{1}{k^2}(E_{L_3}/E_{M_1}), \quad . \quad . \quad . \quad . \quad (19)$$

where $k^2 = \sqrt{2}$. The numerical values are given in Table V.

TABLE V.

	Platinum.	Per cent. difference.	Gold.	Per cent. difference.
$J(L_1/M_1)$…………	4·26	0·9	4·25	1·2
(E_{L_1}/E_{M_1})…………	4·22		4·20	
$J(L_2/M_1)$…………	3·41	0·9	3·37	0·0
$\frac{1}{k}(E_{L_2}/E_{M_1})$…………	3·38		3·37	
$J(L_3/M_1)$…………	2·49	0·4	2·52	2·9
$\frac{1}{k^2}(E_{L_3}/E_{M_1})$…………	2·48		2·45	

These equalities may have no theoretical significance whatever, but as (17) appears to be true for all cases so far examined, any simple relations holding for one or two cases between the L_2 and L_3 jumps and the corresponding energy-level ratios seem worthy of notice.

No theory of absorption so far available appears capable of furnishing the magnitudes of either the K or L jumps with a reasonable degree of accuracy, but as pointed out recently by Richtmyer[(11)], the actual increase in absorption coefficient at the K-absorption edge is given to a fair degree of approximation by the theory of L. de Broglie[(12)]. The theory is equally successful in this respect for the L discontinuities of platinum and gold, although it gives values considerably too large for the ratios that constitute the absorption jumps. L. de Broglie's expression for the part of the atomic fluorescent absorption coefficient due to the electrons of the energy level E_x, where x stands for K, L, or M, etc., is

$$\tau_{ax} = (\pi e^2/mh^2c^4) \,.\, n_x \,.\, E_x^2 \,.\, \lambda^3, \quad \text{where } \lambda \ngtr \lambda_x. \quad . \quad (20)$$

The ratios of the absorption coefficients at the L-absorption edges should be, when scattering is negligible.

$$J_{L_3} = \frac{n_{L_3}E_{L_3}^2 + n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots}{n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots},$$

$$J_{L_2} = \frac{n_{L_2}E_{L_2}^2 + n_{L_3}E_{L_3}^2 + n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots}{n_{L_3}E_{L_3}^2 + n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots},$$

$$J_{L_1} = \frac{n_{L_1}E_{L_1}^2 + n_{L_2}E_{L_2}^2 + n_{L_3}E_{L_3}^2 + n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots}{n_{L_2}E_{L_2}^2 + n_{L_3}E_{L_3}^2 + n_{M_1}E_{M_1}^2 + n_{M_2}E_{M_2}^2 + \dots}$$

The calculated values in Table VI. are obtained with the aid of the table of energy levels in Siegbahn's book and by assuming Stoner's (13) distribution of electrons among the energy levels.

TABLE VI.

		J_{L_1}.	J_{L_2}.	J_{L_3}.
Platinum...	Experimental	1·25	1·37	2·47
	Calculated...	1·39	1·54	5·43
Gold	Experimental	1·26	1·36	2·53
	Calculated	1·38	1·54	5·40

Few other experimental values of the L-absorption jumps are available for comparison. In the paper in which he gave his absorption theory, L. de Broglie quoted without details the following as experimental values for platinum: $J_{L_1}=1·4$, $J_{L_2}=1·63$, $J_{L_3}=2·7$. A. Dauvillier (14) has made measurements on gold, using both ionization and photographic methods. Assuming a λ^3 law, he has apportioned the mass absorption coefficient at L_1 among the different electron groups as in Table VII.

TABLE VII.

Electron group.	M+N+O etc.	L_3.	L_2.	L_1.
Portion of μ/ρ......	42	62	41	35

No other experimental figures are given, but the corresponding values of the absorption jumps would be $J_{L_1}=1·24$, $J_{L_2}=1·39$, $J_{L_3}=2·48$.

The increase in absorption coefficient at the absorption edge should be given directly by expression (20), which may be simplified to

$$\tau_{a_x}=(\pi e^2/mc^2)n_x\lambda_x. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Calculated and experimental values are compared in Table VIII., and in view of the simplicity of expression (21), the agreement seems undoubtedly good, and lends support to Stoner's scheme of electron distribution.

L. de Broglie's theory undoubtedly gives with fair approximation the absorption produced by an electron at the critical wave-length at which it begins to absorb. It can give only very approximately the ratios of the absorption coefficients at the K and L edges, as it supposes absorption to fall off with decreasing wave-length according to the cube law, and for the L and M electrons the absorption does not fall off as fast as this. The values of the ratios determined from the theory are in consequence all larger than those found experimentally.

The absorption of platinum and gold on both sides of the L discontinuities was measured by Allen, who obtained for platinum the equation $\tau/\rho=345\,\lambda^{2\cdot92}$ corresponding to (9), and $\tau/\rho=65\,\lambda^{2\cdot92}$ and $\tau/\rho=66\,\lambda^{2\cdot6}$ corresponding to (12). and for gold, $\tau/\rho=360\,\lambda^{2\cdot92}$ corresponding to (13), and $\tau/\rho=69\,\lambda^{2\cdot92}$ and $\tau/\rho=70\,\lambda^{2\cdot6}$ corresponding to (16). Allen has thus assumed a break in the absorption curve at 1·1 Å.U. for both platinum and gold. In view, however, of the author's results for the absorption between the two L edges nearest $\lambda=1\cdot1$ Å.U. (equations (11) and (15)), where for both platinum and gold the index is much more nearly 2·6 than 2·9, it would appear improbable that any break at 1·1 A.U. really occurs. Allen's equations with index 2·6 for the M absorption agree well with equations (12) and (16), but his equations for the L absorption depart very considerably from (9) and (13) giving higher values of μ/ρ. The experimental values (figs. 3 and 4) found by Allen for the L absorption in this region are, however, for both platinum and gold in much nearer agreement with (9) and and (13). Values from Jonsson's Tables (figs. 3 and 4) are everywhere considerably higher for both platinum and gold than those given by equations (9), (12), (13), and (16), except between 1·5 and 2 Å.U.

TABLE VIII.

Element.	Absorption edge.	Wave-length.	Assumed number of electrons.	Increase in absorption coefficient.	
				L. de Broglie's theory.	Experimental.
Platinum	L_1	0·892	2	50·3	41
	L_2	0·932	2	52·5	50
	L_3	1·070	4	120·4	115
Gold ...	L_1	0·861	2	48	41·6
	L_2	0·901	2	50	48·2
	L_3	1·038	4	116	118·7

Copper.

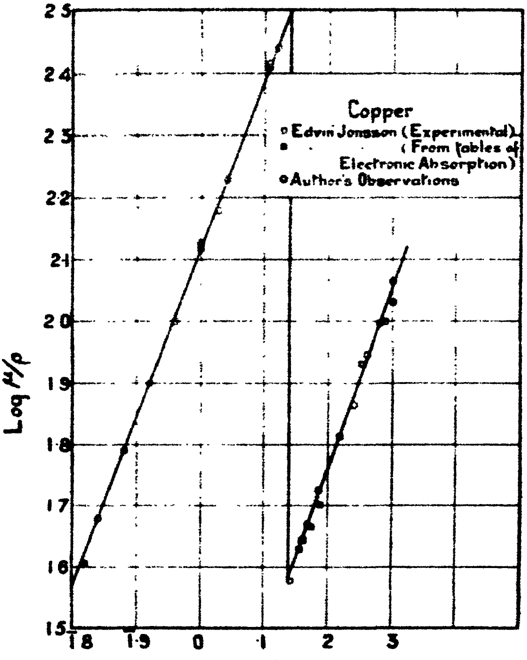
Results for copper are shown in Table II. and fig. 5. The wave-length range includes the K-absorption edge, and the equations found are

$$\log\mu/\rho = 2\cdot116+2\cdot72\log\lambda,\quad . \quad . \quad . \quad . \quad (22)$$

$$\log\mu/\rho = 1\cdot173+2\cdot95\log\lambda.\quad . \quad . \quad . \quad (23)$$

The ratio J_K of the absorption coefficients at the K edge is 8·15, and the increase in μ/ρ is 276. On the theory of L. de Broglie the ratio should be about 20 and the increase in μ/ρ 239. Jonsson has calculated E_K/E_{L_1} to be 8·23, and found 8·2 experimentally for J_K. It is particularly noteworthy that the slope of the K-absorption curve in the neighbourhood of the K edge on a (log μ/ρ, log λ) graph is considerably less than the slope of the L curve near the K edge. Richtmyer and Warburton[15] found that copper accurately followed the cube law between 0·12 Å.U. and 0·30 Å.U., but concluded that the law did not hold near the K edge. Allen obtained the equation $\tau/\rho = 132\lambda^{2\cdot70}$ for wave-lengths between 0·85 Å.U. and the K edge, and L. H Martin found 2·8 as the index. Alexander, who attributed the departure from the simple cube law to multiple ionization, found experimentally the equation $\mu/\rho = 128\cdot8\lambda^3 + 6\cdot0$ near the K edge.

Fig. 5.



Values for copper calculated from Jonsson's tables are in good agreement with equation (22) above, and are shown in fig. 5. Most of the available data for copper agree in giving a relation between μ/ρ and λ for the K absorption near the K edge which cannot be expressed accurately by an equation of the form $\mu/\rho = a\lambda^3 + \sigma/\rho$, where by σ/ρ is meant the actual mass scattering coefficient.

On the other hand, the part of the L-absorption curve near the K edge shows a very near approach to the cube law and, in fact, between the K edge and 2 Å.U. could just be represented by it within experimental error, although the best fit to the data in Table X. is provided by equation (23). For this region of wave-length, Allen found the equation $\tau/\rho = 14{\cdot}5\,\lambda^{2{\cdot}92}$ and Martin $\mu/\rho = 14{\cdot}1\,\lambda^3$, both in near agreement with above. Jonsson's tables give for any element on a ($\log\mu/\rho$, $\log\lambda$) graph an absorption curve the slope of which decreases everywhere with increase of λ, and the curve for copper, although coinciding very closely with that given by equation (22) from $\log\lambda = \bar{1}{\cdot}8$ up to the K edge, shows no increase in slope between the K edge and $\log\lambda = 0{\cdot}3$ to correspond to equation (23). Jonsson's experimental points (fig. 5) show, however, quite good agreement with equation (23), and the best straight line through them would have a slope slightly greater than 2·95. On the whole it seems, therefore, that the average electronic absorption cannot be accurately the same function of $N\lambda$ for all elements, although it would appear to be very nearly so.

Summary.

A description is given of a form of X-ray tube convenient for absorption measurements with homogeneous radiation in the neighbourhood of 1 Å.U., and the results are given of measurements with silver, aluminium, platinum, gold, and copper for wave-lengths between 0·63 and 2 Å.U. The relation between absorption and wave-length was nowhere found to conform exactly to the cube law, the departure from this law often being very considerable. The question is considered as to the possible existence of discontinuities due to multiple ionization. No general law has been found that would fit accurately the data obtained for all the elements examined, although that found recently by Edvin Jonsson appears to furnish a good approximation. The K-absorption jump of copper and the L-absorption jumps of platinum and gold were measured, and the results are compared with theory.

In conclusion the author wishes to thank Dr. Kaye, the Superintendent of the Physics Department, for the provision of facilities for this research, and especially for his continued interest.

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XL. *On the Interpretation of X-Ray Crystal Photographs.*— Part I. *Use of Photographic Grids. By* Wm. H. George, *M.Sc., Ph.D., F.Inst.P., Assistant Lecturer in Physics in the University of Leeds* *.

[Plate VI.]

SUMMARY.

THE paper describes a *photographic grid method*, applicable to any X-ray spectrometer, of measuring X-ray photographs. The photographic plate or film is supported in the X-ray camera (*e.g.*, fig. 1) *entirely* by geometric constraints. A flash of light, together with a printing frame (fig. 2), also fitted with geometric constraints, is used to impress upon the X-ray photograph an image of some network suitable for the interpretation of the particular type of X-ray photograph. A single calibration photograph is taken, and used to fix accurately the geometric

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* Communicated by Prof. R. Whiddington, F.R.S.

constraints of the printing frame. Any subsequent photograph then shows on development both the X-ray photograph and a correctly aligned interpretative grid (*e.g.*, fig. 3, Pl. VI.).

Various modified applications of the method in X-ray crystallography are discussed, and also the application of grid methods to research in subjects other than X-ray crystallography.

IN all research work much time has to be spent upon tasks which do not demand creative thought, and it is usually best to carry out these tasks by almost any adequate method which occurs to the worker rather than to spend long periods seeking elegant methods. In the subject of X-ray crystallography the conditions would appear to be different, for here many workers in all parts of the world have to carry out again and again the same type of task.

The first stage in present-day crystal analysis consists in an attempt to determine the space-group of the crystal. A careful analysis of this process shows that whilst the X-ray crystallographic part of the work involves considerable skill and experience, it does not, in general, demand creative thought. We are therefore justified in regarding the worker, whilst he is carrying out this part of the analysis, as an operating machine. The methods here described are the result of a critical examination of the efficiency of this machine.

MEASUREMENT OF X-RAY PHOTOGRAPHS.

An essential part of the interpretation of any crystal X-ray photograph consists in a determination of the position upon the plate or film of the spots or lines which record X-ray diffraction effects produced by planes in the crystal. It is the purpose of the present paper to show how this measurement of photographs can be made by what may be called a *photographic grid method.* A flash of light is used to impress upon the plate or film a correctly-placed latent image of any set of lines or points which may be useful in interpreting the particular type of photograph. On development the sensitive film shows both the X-ray picture and a suitably-placed interpretative grid. A full application of the principle of *geometric constraints* is essential to the method. After an initial calibrating photograph has been taken, the precision required in all subsequent photographs is achieved automatically.

Before describing the essential details, we may note the alternative methods available for the measurement of X-ray crystal photographs.

Direct Measurement.

The photograph may be directly measured by use of dividers, transparent or opaque scales, or a measuring microscope. When these methods are applied to any but the simplest X-ray photograph, they are exceedingly long and tedious. Moreover, the measuring microscope gives an accuracy much greater than is normally required in X-ray crystallography as distinct from that required in X-ray spectroscopy. Its use is needed only for very accurate determination of the size of the unit cell, for which photographs having sharply-defined lines are necessary.

Bernal Method for Rotation Photographs.

The second method, due to Bernal *, is applicable to single crystal rotation photographs when reciprocal lattice theory is to be used for interpreting the results of the measurements. The method as described consists in using an enlarging lantern to project an image of the X-ray photograph on to a chart from which two of the reciprocal lattice cylindrical coordinates of the spot may be directly read. In actual practice the images of many of the spots projected on to the chart cannot be seen. Moreover, if the chart were intended for use in this way, it would have been printed on white opaque paper instead of on tracing paper. The publication of the method in this impracticable form was an oversight, and on the suggestion of Mr. Bernal the best method devised by him is here described.

Four operations are necessary for each photograph:—(i.) An opaque spot of ink is put as near as possible to the centre of each X-ray spot (on the glass side of the negative if a plane plate is used). (ii.) Some optical enlarging device is adjusted to give a magnification of $10/r$ for a plane plate or $5/r$ for a cylindrical film, where r is the distance of the plate or film from the crystal. (iii.) An image of the plate or film is then projected on to a sheet of paper, and again an ink spot is placed as near as possible to the centre of each projected spot. (iv.) The appropriate chart (I. for a plane plate or II. for a cylindrical film), printed on tracing-paper, is then fitted over this projection so that, for as many as possible of the sets of four points (or pairs on the equatorial layer-line), each of the points in a set gives the same reading on the chart.

In actual practice the fitting of the chart is difficult, for even if the plate is truly perpendicular to the X-ray beam and parallel to the axis of rotation of the crystal, the "spotting in" both on the original negative and on its projection, together with the defects of the optical system, introduces errors. These errors are such that the fourfold (or twofold on the zero layer-line) symmetry of the rotation photograph is destroyed. Still greater difficulty is experienced with oscillation photographs, for these have at most only two quadrants alike, whilst the most general type (little used at present) have all four quadrants different.

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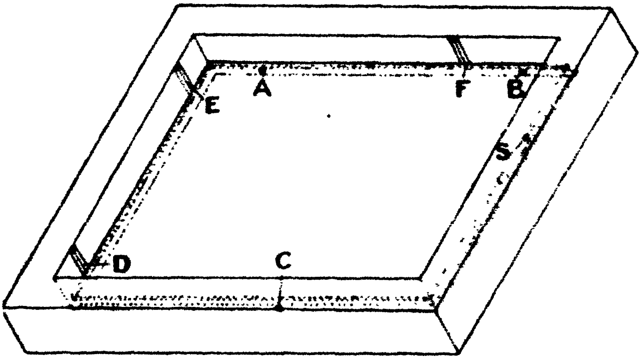
* Proc. Roy. Soc. A, cxiii. p. 130 (1926).

In the methods now to be described all these operations, and the consequent errors introduced by them, are eliminated. The accuracy attained is equal to that of any of the other methods, with the exception of the use of the travelling microscope in the measurement of sharply defined lines, such as are obtained in spectroscopy.

Fig. 1.



Typical plane-plate X-ray camera fitted with six geometric constraints.

PHOTOGRAPHIC GRID METHOD.

In adopting the photographic grid method, two modifications of the X-ray apparatus are normally required. The first is an addition to the X-ray camera of three geometric constraints or their equivalent. The second is the preparation of a printing-frame.

Modification of X-Ray Camera.

(i.) *Plane Plate.*

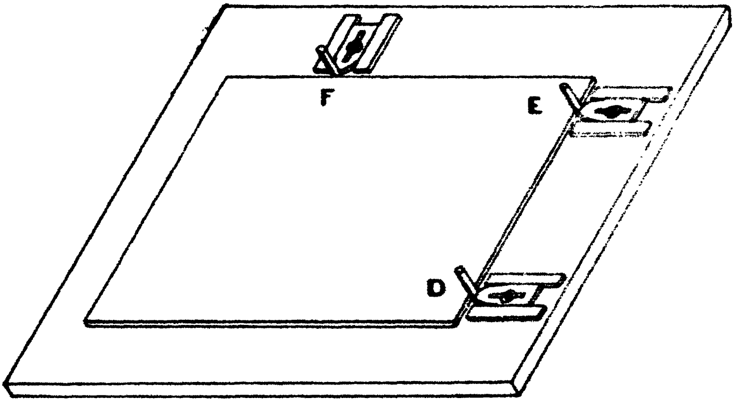
In all types of photographic spectrometer the plate-holder of the X-ray camera is provided with three geometric constraints (*e. g.*, three spherical-ended screws, ABC of fig. 1) or their equivalent, on to which the sensitive film of the photographic plate is pressed by a spring or by gravity. By this means the distance of the sensitive film from the crystal is known from an initial calibration of the instrument. However, with this arrangement the plate still has three degrees of freedom. If the grid method is to be used, these three remaining degrees of freedom must be removed by the addition to the camera of three more constraints acting upon two edges of the plate. For example, three steel rods or agate knife-edges may be fixed inside the camera at DEF of fig. 1. The spring (S) serves to keep the plate pressed against the constraints (DE). A spring opposite to F has not been found necessary. So long as the principle of removing the remaining three degrees of freedom of the plate is obeyed, the constraints may be added in any convenient way, and it is usually quite unnecessary to have a new camera made Care must be taken that the constraints stand out far enough to prevent any irregularity in the edge of the plate from touching the interior of the camera. That is, even the most roughly cut photographic plate must be supported *solely* by the six constraints, ABCDEF.

Calibration Photograph.—When these additions have been made to whatever type of plate-holder is used, the camera is loaded with a plate pressed against the six constraints, and a complete rotation photograph is taken by rotating about the needle axis any fine needle-shaped crystal which gives good body reflexions of X-rays. The crystal should be carefully *centred* so as to give some sharply-defined narrow black spots on the photograph, which is required as a calibration photograph determining once and for all the relative positions of the three constraints DEF and the axis of rotation or support of the crystal on the spectrometer. A Laue photograph might also be used as a calibration photograph.

(ii.) *Cylindrical Camera.*

The modification necessary to the ordinary cylindrical camera will be clear if the following details are noted. It will be found that the edges of commercial films are straight to a high order of accuracy. To the bottom of the X-ray cylindrical camera is added a narrow horizontal rim perpendicular to the sides of the cylinder, and in loading the camera the X-ray film is always pushed down so that its bottom edge rests on this ledge (1 mm. wide or so). The film is then rotated round inside the cylinder until one of the vertical edges touches a stop. This stop may be a cylindrical metal pin pushed radially through the side of the cylindrical camera wall at a height (*d*) above the bottom of the film, of about half the width of the film. An opaque black paper envelope having three sides sealed should be prepared for permanent use. One of its dimensions should be about 1 mm. less than the height of the particular size of film used, and at one edge a small hole should be cut at height (*d*) above the bottom of the film. This ensures that the bottom edge of the film and the point of a vertical edge actually touch the constraints provided. As a minor point, it may be noted that errors due to distortion of the film caused by a wrinkled black paper envelope may be avoided by preparing the envelope upon a cylinder and allowing the gum or paste to dry whilst the envelope is still on the cylinder. This envelope is, of course, necessary whether or no the grid method is used.

Fig. 2.



Printing-frame fitted with three geometric constraints.

As before, a calibration photograph must be taken for use in setting the constraints of the printing-frame.

We come now to the second modification necessary when the grid method is to be adopted.

Initial Preparation of the Printing-frame.

Fig. 2 shows a convenient form of printing-frame. This consists of a brass frame into which is sealed permanently a glass plate, the *grid*, the preparation of which is dealt with in the following section. Three constraints, DEF, consisting again of steel cylinders or agate knife edges perpendicular to the plane of the grid, are initially adjustable in a direction perpendicular to the edge of the plate. Since the edges of commercial plates and films are *not* straight edges *mutually perpendicular*, it is essential that the *constraints in the printing-frame touch the same points of the X-ray plate or film as do those in the X-ray camera.*

The final stage in the initial preparation of the printing-frame consists in brightly illuminating the grid from below and carefully adjusting, relative to it, the calibrating X-ray photograph. When this has been done, the constraints of the frame are moved up to touch the edges of the plate or film, and are there screwed down firmly. Spring washers under the screw-heads facilitate the adjustment. The X-ray photograph having been removed, the printing-frame is then ready for use.

Preparation of Grid.—The grid consists of a glass plate having a relatively opaque background and transparent lines or spots. Its method of preparation depends mainly upon the nature of the lines or spots, and this in turn depends upon the theoretical method to be adopted for interpreting the measurements made upon the photograph. We will assume that the choice of network has been made. Simple networks such as sets of straight lines or circles can be machine-ruled.

A more widely applicable method consists in using a good camera, such as is used for preparing lantern-slides, to prepare the grid photographically. The network should be drawn on a large scale with Indian ink upon white Bristol board or good tracing-cloth, the width of the lines used being such that fine lines are obtained upon the grid with the particular scale of reduction used. The drawing should be brightly illuminated with as uniform a distribution of intensity as possible so as to give uniform opacity to the background of the grid. Drawings upon tracing-cloth may be illuminated from behind through an opal glass screen, and any drawing should be so aligned relative to the camera that the centre of the network is about 1 mm. off the centre of the photographic plate. This ensures that when the grid has been sealed in the routine-brass printing-frame the X-ray plate will overhang the edges of the grid by about 1 mm., and so permit contact with the three geometric constraints.

In photographic preparation of grids, slow-process plates should be used and development should be carried out slowly in a hydroquinine developer. In brief, the technique of the antern-slide maker should be used. As these photographic grids are required for permanent use, great care should be taken to fix and wash them thoroughly. It would probably be convenient to protect the film side with a coat of suitable varnish, although the writer has used an unprotected grid for one year without producing in it any appreciable signs of wear.

If reciprocal lattice theory is to be used for the interpretation of rotation or oscillation X-ray photographs, one or other of the Bernal (*ibid.*) charts should be used in preparing a suitable grid. For a plane plate, Chart I. should be photographed with a reduction of $10/r$, and for a cylindrical film, Chart II. with a reduction of $5/r$, where r is the distance in cm. from the crystal to the sensitive film. An example of the use of a grid, prepared from Chart II., is shown in Pl. VI. (fig. 3).

If measurements upon an X-ray photograph are required in cms., quite good grids can be prepared by the use of the old-fashioned engraved graph paper. Examples of the use of such grids are reproduced elsewhere *. They were there used for research in acoustics.

Routine Use of Printing-frame.—When the grid has been prepared and sealed into the printing-frame and the three constraints, DEF, have been permanently screwed down by aid of the calibration photograph, the printing-frame is ready for routine use. It is convenient to fix it horizontally over a hole in the bench in the photographic dark-room, and at about 1 metre below it a pocket flash-lamp bulb and battery should be fixed and connected to a tapper- or morse-key on the bench.

When the X-ray camera is to be loaded with a *plane plate*, the photographic plate is first placed film side downwards on to the grid, and is pushed up to the constraints, DEF of fig. 2. The key is then tapped for a fraction of a second, and the plate is placed against the constraints of the camera (fig. 1), the image of the grid remaining latent during the X-ray exposure. If preferred, this printing of the grid may, of course, be done after the X-ray exposure, just before the plate is put in the developing-dish. The complete operation does not occupy more than 2–5 seconds. The tapping of a key does not provide a fine adjustment of the exposure to light, but in practice it is quite as accurate as is necessary. Each worker gets used to tapping so as to give, on development, lines of the intensity which suits him best. For example, if he anticipates giving an over exposure to X-rays the flash of light should be longer, since the plate will not be developed for so long. The flash-lamp can be covered with one or more layers of white tissue paper if it is too bright. The plates used by the writer seem to need a shorter exposure to light in the grid printing than the films used.

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* George, Phil. Mag. (6) xlvii. p. 591 (1924), xlviii. p. 34 (1924); 'Nature,' cxiii. p. 387 (1924).

When the X-ray camera is to be loaded with a *cylindrical film*, the operations are almost the same as for a plate, except that after the film has been placed on the grid, it should be pressed in contact with the grid before the morse-key is tapped. An old photographic plate covered with black paper is suitable for this purpose. The final pushing of the film on to the constraints of the printing frame should be done *after* the film has been pressed flat. A corner may be cut of the film to identify the edge which has been pressed against the single constraint (*i. e.*, the constraint which is at height *d* above the bottom edge of the film). The film is then put in the envelope, and the camera is loaded as previously described (p. 377). The modifications necessary with the type of cylindrical camera in which the cylindrical form is imposed upon the film by pressing it on to the *outside* of a cylinder will be obvious.

No matter what type of camera be used, it is of the utmost importance to the success of the grid method that the plate or film be supported *solely* by geometric constraints which actually touch the plate or film. The particular type of constraints used is unimportant. The plate or film may be rigidly fixed in some other frame, the edges of which may be used to make contact with the constraints if this is found more convenient.

When the grid method as here described is used, every photograph shows on development both the X-ray photograph and the *correctly-placed* interpretative grid. The coordinates of the spots are read off directly by eye with or without the aid of a low-power large-field lens, whilst the X-ray plate is illuminated from behind by diffused light (*e. g.*, a large sheet of brightly illuminated white blotting-paper having a matt surface, or opal glass illuminated from behind). An example is shown in Pl. VI. (fig. 3). The grid used was prepared from the Bernal Chart II., and the X-ray photograph was prepared by rotating about a cubic axis a diamond (slightly mis-set). In the figure the axis of rotation is horizontal. None of the slight fogging of the film is due to the light used in the grid process, as can be seen by examining the parts of the original film which were protected by metal clips during the X-ray exposure.

The irregular fogging was introduced by the photographic processes used to get a reproduction of black spots on white background so as show the appearance of the original film.

Partial Applications of the Methods.—Various partial applications of the methods here described are of value in special cases.

If it is not desired to have any markings on the X-ray plate except those produced by the X-rays, then a print on to another photographic plate can be made from the grid plate. This print is placed and fitted over each X-ray plate or film in turn so that the sensitive sides are in contact. Several research workers are now using, in this way, grids prepared from the Bernal charts. The objections to this method are that (i.) the fog of the grid plate is added to that of the X-ray plate, (ii.) each X-ray negative needs a new fitting of the chart and is liable to be displaced during use, and (iii.) a layer of glass is always interposed between the observer and the X-ray spots and lines.

For purposes of reproduction an ordinary X-ray negative can be clamped on to one of these glass prints from a grid, and the two together used in the ordinary photographic enlarging lantern *.

The principle of the geometric constraints could be very conveniently applied to work with the measuring microscope, for, by providing three more constraints than usual, every plate to be measured would merely need to be pushed on to the constraints in order to be correctly aligned for the measuring process.

Advantages of the Complete Grid Method.—The grid method, by the use of a single skilled operation (the setting of the three constraints, DEF of fig. 2), entirely replaces the many hundreds of skilled operations carried out by the X-ray crystallographer in one year alone. It therefore saves an appreciable amount of his time and energy. It is not usual to discuss this "efficiency" of the worker in research, but its consideration is forced upon the X-ray crystallographer by the excessive amounts of time he finds himself spending in operations which are neither creative thinking nor operations directly required as the result of such thought.

The negative obtained when the complete grid method is used is, of course, a fuller record than is an ordinary X-ray negative, and it can be interpreted away from laboratories. For example, if a suitable Bernal chart be used to prepare the grid, then a single crystal rotation or oscillation photograph can be interpreted without the interpreter knowing the plate distance or the wave-length of the monochromatic X-rays used to prepare the photograph. In a precision cylindrical camera used for taking a complete rotation photograph, only one-quarter of the usual sized film need be used. For most oscillation photographs (all except the most general, where all four quadrants of the photograph are different), only half the usual size of film is required. In all photographs the "centre" is permanently determined and recorded for the given spectrometer. The writer would suggest that the reproduction in a scientific journal of one-quarter of a single crystal rotation photograph taken with the use of the grid method, would record more information concerning the actual results of the experimental part of the research work relevant to crystal structure determination, than would a table showing the results of very accurate measurements made with a measuring microscope upon the X-ray negative. This statement may appear controversial when one examines some of the papers on crystal structure now published, but it can best be discussed later when the methods of determining indices are treated.

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* Moseley Student's Report to the Royal Society, 1927.

A curious feature is observed when the grid method is used with films. These are coated on both sides with sensitive material, and the X-rays, of course, penetrate through the film, producing a blackening on both sides of the developed record. The light used to print the grid, however, does not penetrate through the first layer of sensitive gelatine. Hence a film taken by the grid method shows in transmitted light both the network and the X-ray photograph, but when it is examined by light reflected from one side only, it shows only the X-ray photograph if the side examined is the one which was not in contact with the grid plate in the printing frame.

Use of Grid Method in other Types of Research.—The grid method could usefully be applied to many types of experimental research work where the same kind of photograph is taken many times. For example, in instantaneous photography, if the film or plate be supported by geometric constraints, then its position relative to the phenomenon being photographed is always the same to a high degree of accuracy. One modification which the writer (*ibid.*) found useful in optical photography consists in incorporating the grid into the apparatus so that a separate printing-frame is unnecessary. This simplification is not possible in X-ray photography nor in optical photography with radiation which would be heavily absorbed by the grid plate. Care must be taken, when this simplified process is used, that the focussing is correct *after* the radiation has passed through the grid plate.

Acknowledgments.

The methods here described were devised whilst I was working as the Moseley Student of the Royal Society at the Davy Faraday Laboratory of the Royal Institution, London. I therefore wish to thank the Royal Society for financial aid and Sir Wm. Bragg and the Managers of the Davy Faraday Laboratory for their generous hospitality there.

It is hoped to deal in Part II. with certain types of rotation photographs taken with the grid method, and in Part III. with moving-film photographs.

XLI. *Note on the Platinum Thermometer Temperature Scale.*

By F. E. Hoare, *B.Sc., A.R.C.S., Assistant Lecturer in Physics, University College of the South-West of England, Exeter* *.

At the Seventh General Conference (1927) of the International Bureau on the International Temperature Scale it was recommended that platinum thermometers should be used for the realization of the absolute scale from the ice point to 660° C., the temperature to be deduced from the formula

$$R_t = R_0(1 + at + bt^2).$$

The constants R_0, a, and b should be determined from the ice, steam, and sulphur points respectively, the purity and physical condition of the platinum being such that the ratio $\frac{R_t}{R_0}$ shall not be less than 1·390 for $t = 100°$ C., and 2·645 for $t = 444·6°$ C. Hence the fixed value of the difference coefficient d, usually taken as $1·5 \times 10^{-4}$, in the equation

$$X = t - pt = d(t - 100)t,$$

where pt is the temperature on the platinum scale, has not been adopted, but must be separately determined for each thermometer.

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* Communicated by Prof. F. H. Newman.

In order that the solution of a large quadratic equation for each temperature may be avoided, it is very convenient in practice to calculate the value of the correction X to be applied to the platinum thermometer temperature, as defined by the equation

$$pt=\frac{R_t-R_0}{R_{100}-R_0}\times 100$$

for any value of the difference coefficient, from tables which give the value of the correction for a certain value of d. This may be done in the following manner.

Consider two platinum thermometers which are at the same temperature as calculated on the platinum scale. Let the difference coefficients for the two thermometers be d and d', and the centigrade temperatures to which the platinum temperature corresponds be t and t' respectively. Then

$$X=t-pt=d\,(t-100)t$$

and

$$X'=t'-pt=d'(t-100)t',$$

where X and X′ represent the corrections to be applied to the first and second thermometers respectively.

Also let

$$t'=t+x \quad \text{and} \quad d'=d+y.$$

Then

$$t+x-pt=(d+y)\,(t-100+x)\,(t+x)\,;$$

and on expanding and substituting $t-pt=d(t-100)t$,

$$x=\frac{yt(t-100)}{1-d'(2t-100+x)}$$

$$=\frac{yt(t-100)}{1-d'(2t-100)},$$

if, as is usually the case in practice, x is small in comparison with $2t-100$.

Therefore

$$x=\frac{yX}{d\{1-d'(2t-100)\}}. \quad . \quad . \quad . \quad . \quad (1)$$

The value of t is directly obtainable from the tables already mentioned, as is also the value of X. Solving this equation for x is a much simpler operation than determining t' from the ordinary quadratic equation.

The temperature t' is given by the equation

$$t'=pt+X+x\,;$$

and if $d'(2t-100)$ is small in comparison with unity, the correction reduces to

$$X'=X+x=\frac{d'}{d}\cdot X,$$

which is the form proposed by Griffiths[*]. This correction is not accurate, and can be used only for the most approximate work.

The relative accuracy of the method given above for finding the correction for any value of d is illustrated in the following table. The second and third columns are the values of the temperature on the centigrade scale, obtained by solving the equations for X and X′, for certain values of pt, using different values for d. The fourth column gives the temperature obtained by using equation (1), assuming $d=1{\cdot}5\times10^{-4}$ and $d'=1{\cdot}6\times10^{-4}$.

	$t°$ C.		
pt.	$d=1{\cdot}5\times10^{-4}$.	$d=1{\cdot}6\times10^{-4}$.	Using equation (1).
197°	200	200·2101	200·2101
470°	500	502·3375	502·3364
1002°	1200	1220·9977	1220·8861

Thus, even at such a high temperature as 1200° C., and using a value of d' which is outside that generally obtained in practice, the correction gives temperatures correct to a tenth of a degree centigrade. The calculations can usually be made with sufficient accuracy on an ordinary slide-rule.

XLII. *On the Thermal Efficiency of Standard Cycles for Internal Combustion Engines.* *By* H. H. JEFFCOTT[†].

Introductory.

1. THE principal object of the present paper is to give an account of a simple method for the calculation of the thermal efficiency of certain standard cycles for internal combustion engines using as the working fluid air or other real gas of which the specific heats vary with the temperature.

Sir Dugald Clerk, in his recent[‡] paper on Standards of

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[*] 'Nature,' liii. p. 45 (1895).

[†] Communicated by the Author.

[‡] Sir Dugald Clerk, "Standards of Thermal Efficiency for Internal Combustion Motors," Min. Proc. Inst. C.E. ccxxv. p. 279 (1928).

Thermal Efficiency, states that "the time has come for the application of accumulated knowledge to the substitution of real working fluids for the ideal properties which were necessary because of ignorance of the real." In the following pages the working fluid will ordinarily be supposed to be air, but the method will be developed so as to be of general application.

2. The symbols used are as follows :—

The suffixes 1, 2, 3, 4 refer to the four corners of the indicator diagram, and correspond respectively to the commencement of compression of the charge, the end of compression, the end of ignition or commencement of expansion, and the end of expansion or commencement of discharge.

p	represents the	pressure of the working fluid.
v	,, ,,	volume of the working fluid.
t	,, ,,	temperature of the working fluid, ° C.
T, T′	,, ,,	temperature of the working fluid, ° C. absolute.
C_p	,, ,,	specific heat of the working fluid at constant pressure in heat units.
,,	,, ,,	specific heat of the working fluid at constant volume in heat units.
R	,, ,,	gas constant.
γ	,, ,,	ratio $\frac{C_p}{C_v}$ for the working fluid.
H	,, ,,	total heat of the working fluid at T, p, and v.
η	,, ,,	thermal efficiency of the cycle.
r	,, ,,	ratio of compression $\frac{v_1}{v_2}$.
r'	,, ,,	ratio of expansion $\frac{v_4}{v_3}$.
ρ	,, ,,	ratio $\frac{v_3}{v_2}$.
ρ'	,, ,,	ratio $\frac{v_4}{v_1}$.
σ	,, ,,	ratio $\frac{p_3}{p_2}$ in cycle V.

$\phi(T)$ and $\psi(T)$ represent functions of T defined in paragraphs 6 and 7.

$a', a, b, e \ldots k, l, m$ represent various numerical constants.

3. We shall consider five different ideal cycles on the pressure-volume diagram. The principal features are indicated in figs. 1–5.

All these cycles are made up of adiabatics, and of straight lines on the diagrams. For all cycles the thermal efficiency is measured by

$$\frac{\text{Heat input} - \text{Heat rejected}}{\text{Heat input}}.$$

4. The specific heats of gases at constant pressure and at constant volume vary with the temperature, and the extent of this variation can exercise an important influence on the thermal efficiencies of ideal cycles of the kind here considered. For the working fluids met with in practice, the specific heat may be represented with close approximation by an algebraical expression in ascending powers of T, where T represents the absolute temperature. Thus we can find appropriate values of the coefficients a, b, c ..., so that

$$C_v = a + bT + cT^2 + \dots$$

is a close approximation. The difference of the specific heats $C_p - C_v$ is approximately constant, and accordingly

$$C_p = a' + bT + cT^2 + \dots$$

so that

$$a' - a = C_p - C_v = R.$$

We are justified in using an algebraical expression of this kind, for the coefficients can be chosen so that the values of the specific heats calculated therefrom will lie within the probable errors of the experimental values corresponding to the various values of the temperature that fall within the range to be considered. Moreover, we propose to apply to such approximate representation the process of integration only, and not differentiation, so that mathematically we are on safe ground.

5. It is necessary to employ the fundamental relation for gases connecting pressure, volume, and temperature. In this investigation the simple approximate relation

$$pv = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

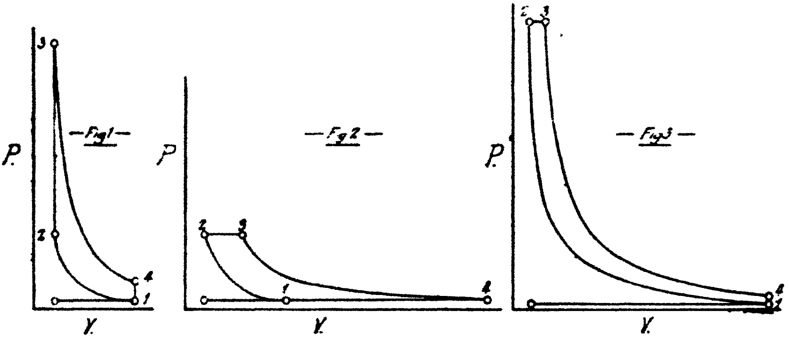
will be sufficiently exact for our purpose, having regard to the ranges of temperature and pressure involved.

Other equations have been proposed by various workers more accurately representing the relation of pressure, volume, and temperature for various gases, notably those suggested by van der Waals, Clausius, Boltzmann, Berthelot, Kamerlingh Onnes, Dieterici, and Wohl. Thus van der Waals's equation is of the form

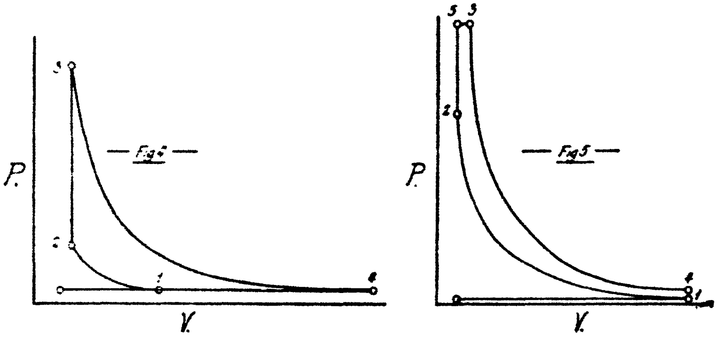
$$\left(p+\frac{\alpha}{v^2}\right)(v-\beta) = \mathrm{RT},$$

where α refers to the cohesive forces between the molecules, and β refers to the volume occupied by them.

Figs. 1-5.



Figs. 4 & 5.



When the pressure is measured in atmospheres, and the volume is unity at 0° C. and one atmosphere pressure, then for air $\alpha = \cdot 00257$ and $\beta = \cdot 00209$, or, according to some observers, $\beta = \cdot 00156$.

Having regard to the degree of accuracy required for our present purpose, and to the values of p and T involved, it will be seen that the simpler equation $pv = \mathrm{RT}$ is a sufficiently close approximation for the behaviour of the gas.

6. *Equation to Adiabatic.*—The adiabatic on the pressure-volume diagram is conditioned by the fact that no external heat is transmitted to or taken from the working fluid in passing from one point to another on the adiabatic curve. In particular we consider two adjacent points on the curve of which the coordinates are p, v and $p+dp$, $v+dv$, the corresponding temperatures being T and $T+dT$. The increment of heat dH added to or taken away from the working fluid is measured by $C_v dT+p\,dv$, since $C_v dT$ represents the change of internal energy of the gas, and $p\,dv$ is the work done in its expansion.

For every consecutive pair of points on the adiabatic this increment must be zero. Accordingly we have

$$dH = C_v dt + p\,dv = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Also

$$pv = RT.$$

Hence

$$C_v \frac{dT}{T} + R\frac{dv}{v} = 0.$$

Therefore

$$\int C_v \frac{dT}{T} + R\log_e v = k,$$

where k is a constant of integration.

Now

$$C_v = a + bT + cT^2 + \ldots .$$

Hence, on integrating,

$$a\log_e T + bT + \frac{c}{2}T^2 + \ldots + R\log_e v = k.$$

Let $\phi(T)$ represent

$$a\log_e T + bT + \frac{c}{2}T^2 + \ldots .$$

Hence, for an adiabatic,

$$\phi(T) + R\log_e v = k.$$

If v_1, T_1 and v_2, T_2 be the volumes and temperatures at two points on the same adiabatic,

$$\phi(T_2) - \phi(T_1) + R\log_e v_2 - R\log_e v_1 = 0.$$

Representing $\frac{v_1}{v_2}$ by r, this becomes

$$\phi(T_2) - \phi(T_1) = R\log_e r. \quad . \quad . \quad . \quad . \quad (3)$$

In like manner we obtain for the adiabatic, through v_3, T_3 and v_4, T_4,

$$\phi(T_3)-\phi(T_4)=R\log_e r', \quad . \quad . \quad . \quad . \quad (4)$$

where

$$r'=\frac{v_4}{v_3}.$$

In passing, we observe that, if $b=c=\ldots=0$,

$$\log_e T_2-\log_e T_1=\frac{R}{a}\log_e\frac{v_1}{v_2},$$

and as $\frac{R}{a}=\gamma-1$, this reduces to

$$p_2v_2^{\gamma}=p_1v_1^{\gamma},$$

which is the equation to the adiabatic when C_p and C_v are constant.

7. We next consider the heat put in or abstracted along one of the straight lines of the pressure-volume diagram. For the sake of generality we shall take a line oblique and having as its equation

$$p=lv+m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As in paragraph 6, the increment of heat dH added in passing from p, v to $p+dp$, $v+dv$ is

$$dH=C_v dT+p\,dv, \quad . \quad . \quad . \quad (6)$$

and the total heat added in raising the temperature from T_2 to T_3 and the volume from v_2 to v_3 is

$$H_3-H_2=\int_{T_2}^{T_3}C_v dT+\int_{v_2}^{v_3}p\,dv.$$

Now
$$\int C_v dT=\int(a+bT+cT^2+\ldots)dT$$

$$=aT+\frac{b}{2}T^2+\frac{c}{3}T^3+\ldots$$

$$=\psi(T) \quad \text{say.}$$

Also
$$\int_{v_2}^{v_3}p\,dv=\int_{v_2}^{v_3}(lv+m)\,dv$$

$$=\frac{l}{2}(v_3^2-v_2^2)+m(v_3-v_2)$$

Since $pv=RT$, we have $v(lv+m)=RT$, and as this is true for the points v_2, T_2 and v_3, T_3, we find

$$\frac{l}{2}(v_3^2-v_2^2)+m(v_3-v_2)=\tfrac{1}{2}R(T_3-T_2)+\tfrac{1}{2}R\left(T_2\frac{v_3}{v_2}-T_3\frac{v_2}{v_3}\right).$$

Put $\dfrac{v_3}{v_2}=\rho$, and we have

$$\int_{v_2}^{v_3}p\,dv=\tfrac{1}{2}R(T_3-T_2)+\tfrac{1}{2}R\left(T_2\rho-\frac{T_3}{\rho}\right).$$

Hence, finally,

$$H_3-H_2=\psi(T_3)-\psi(T_2)+\tfrac{1}{2}RT_3\left(1-\frac{1}{\rho}\right)-\tfrac{1}{2}RT_2(1-\rho). \quad (7)$$

The heat rejected H_4-H_1 between the temperatures T_4 and T_1 is found in like manner to be represented by the expression

$$H_4-H_1=\psi(T_4)-\psi(T_1)+\tfrac{1}{2}RT_4\left(1-\frac{1}{\rho'}\right)-\tfrac{1}{2}RT_1(1-\rho'). \quad (8)$$

The thermal efficiency η is then

$$\eta=\frac{(H_3-H_2)-(H_4-H_1)}{H_3-H_2}. \quad . \quad . \quad . \quad (9)$$

8. The values of r, r' ; ρ, ρ' may now be written down for the various types of cycle:—

I. $\rho=\rho'=1,\qquad r=r'$;

II. $\rho=\dfrac{T_3}{T_2},\qquad \rho'=\dfrac{T_4}{T_1},\qquad \dfrac{r}{r'}=\dfrac{\rho}{\rho'}$;

III. $\rho=\dfrac{T_3}{T_2},\qquad \rho'=1,\qquad \dfrac{r}{r'}=\rho$:

IV. $\rho=1,\qquad \rho'=\dfrac{T_4}{T_1},\qquad \dfrac{r'}{r}=\rho'$;

V. $\rho\sigma=\dfrac{T_3}{T_2},\qquad \rho'=1,\qquad \dfrac{r}{r'}=\rho$.

9. Substituting these values in H_3-H_2 and H_4-H_1, we have

I. Constant volume admission, constant volume rejection:

$$H_3-H_2=\psi(T_3)-\psi(T_2),$$
$$H_4-H_1=\psi(T_4)-\psi(T_1);$$

II. Constant pressure admission, constant pressure rejection:

$$H_3 - H_2 = \psi(T_3) + RT_3 - \psi(T_2) - RT_2,$$

$$H_4 - H_1 = \psi(T_4) + RT_4 - \psi(T_1) - RT_1.$$

III. Diesel—constant pressure admission, constant volume rejection:

$$H_3 - H_2 = \psi(T_3) + RT_3 - \psi(T_2) - RT_2,$$

$$H_4 - H_1 = \psi(T_4) - \psi(T_1).$$

IV. Atkinson — constant volume admission, constant pressure rejection:

$$H_3 - H_2 = \psi(T_3) - \psi(T_2),$$

$$H_4 - H_1 = \psi(T_4) + RT_4 - \psi(T_1) - RT_1.$$

V. Dual—constant volume admission followed by constant pressure admission, constant volume rejection. Here we include in $H_3 - H_2$ the heat input up to the corner (5) of the diagram. Then

$$H_3 - H_2 = \psi(T_3) + RT_3\left(1 - \frac{1}{\rho}\right) - \psi(T_2),$$

$$H_4 - H_1 = \psi(T_4) - \psi(T_1).$$

10. The thermal efficiency of any of the cycles considered may be obtained with the aid of equations (3), (4), (7), (8), (9), and the appropriate relations in paragraph 8.

Usually the efficiency can be expressed in terms of three of the quantities involved, such as T_2, T_3, r; but in cycle V the value of σ is also required.

The solution of these equations is not very troublesome, but the graphical process now to be described leads with great rapidity to the desired result.

Two diagrams are required, preferably drawn on squared paper. On the first (fig. 6) are plotted values of $\phi(T)$ as ordinates against corresponding values of T as abscissæ. Also on this diagram a curve is plotted giving as ordinates $R \log_e r$ against r as abscissæ.

On the second diagram (fig. 7) are plotted values of $\psi(T)$ as ordinates against corresponding values of T as abscissæ. Also a second curve is plotted to represent $\psi(T) + RT$. To save space, both these curves are shown on the second diagram, instead of having a separate figure for each type of

Since $pv=RT$, we have $v(lv+m)=RT$, and as this is true for the points v_2, T_2 and v_3, T_3, we find

$$\frac{l}{2}(v_3^2-v_2^2)+m(v_3-v_2)=\tfrac{1}{2}R(T_3-T_2)+\tfrac{1}{2}R\left(T_2\frac{v_3}{v_2}-T_3\frac{v_2}{v_3}\right).$$

Put $\frac{v_3}{v_2}=\rho$, and we have

$$\int_{v_2}^{v_3} p\,dv=\tfrac{1}{2}R(T_3-T_2)+\tfrac{1}{2}R\left(T_2\rho-\frac{T_3}{\rho}\right).$$

Hence, finally,

$$H_3-H_2=\psi(T_3)-\psi(T_2)+\tfrac{1}{2}RT_3\left(1-\frac{1}{\rho}\right)-\tfrac{1}{2}RT_2(1-\rho). \quad (7)$$

The heat rejected H_4-H_1 between the temperatures T_4 and T_1 is found in like manner to be represented by the expression

$$H_4-H_1=\psi(T_4)-\psi(T_1)+\tfrac{1}{2}RT_4\left(1-\frac{1}{\rho'}\right)-\tfrac{1}{2}RT_1(1-\rho'). \quad (8)$$

The thermal efficiency η is then

$$\eta=\frac{(H_3-H_2)-(H_4-H_1)}{H_3-H_2}. \quad . \quad . \quad . \quad (9)$$

8. The values of r, r'; ρ, ρ' may now be written down for the various types of cycle:—

I.	$\rho=\rho'=1,$		$r=r'$;
II.	$\rho=\frac{T_3}{T_2},$	$\rho'=\frac{T_4}{T_1},$	$\frac{r}{r'}=\frac{\rho}{\rho'}$;
III.	$\rho=\frac{T_3}{T_2},$	$\rho'=1,$	$\frac{r}{r'}=\rho$ ·
IV.	$\rho=1,$	$\rho'=\frac{T_4}{T_1},$	$\frac{r'}{r}=\rho'$;
V.	$\rho\sigma=\frac{T_3}{T_2},$	$\rho'=1,$	$\frac{r}{r'}=\rho.$

9. Substituting these values in H_3-H_2 and H_4-H_1, we have

I. Constant volume admission, constant volume rejection:

$$H_3-H_2=\psi(T_3)-\psi(T_2),$$
$$H_4-H_1=\psi(T_4)-\psi(T_1);$$

II. Constant pressure admission, constant pressure rejection :

$$H_3 - H_2 = \psi(T_3) + RT_3 - \psi(T_2) - RT_2,$$

$$H_4 - H_1 = \psi(T_4) + RT_4 - \psi(T_1) - RT_1.$$

III. Diesel—constant pressure admission, constant volume rejection :

$$H_3 - H_2 = \psi(T_3) + RT_3 - \psi(T_2) - RT_2,$$

$$H_4 - H_1 = \psi(T_4) - \psi(T_1).$$

IV. Atkinson — constant volume admission, constant pressure rejection :

$$H_3 - H_2 = \psi(T_3) - \psi(T_2),$$

$$H_4 - H_1 = \psi(T_4) + RT_4 - \psi(T_1) - RT_1.$$

V. Dual—constant volume admission followed by constant pressure admission, constant volume rejection. Here we include in $H_3 - H_2$ the heat input up to the corner (5) of the diagram. Then

$$H_3 - H_2 = \psi(T_3) + RT_3\left(1 - \frac{1}{\rho}\right) - \psi(T_2),$$

$$H_4 - H_1 = \psi(T_4) - \psi(T_1).$$

10. The thermal efficiency of any of the cycles considered may be obtained with the aid of equations (3), (4), (7), (8), (9), and the appropriate relations in paragraph 8.

Usually the efficiency can be expressed in terms of three of the quantities involved, such as T_2, T_3, r ; but in cycle V the value of σ is also required.

The solution of these equations is not very troublesome, but the graphical process now to be described leads with great rapidity to the desired result.

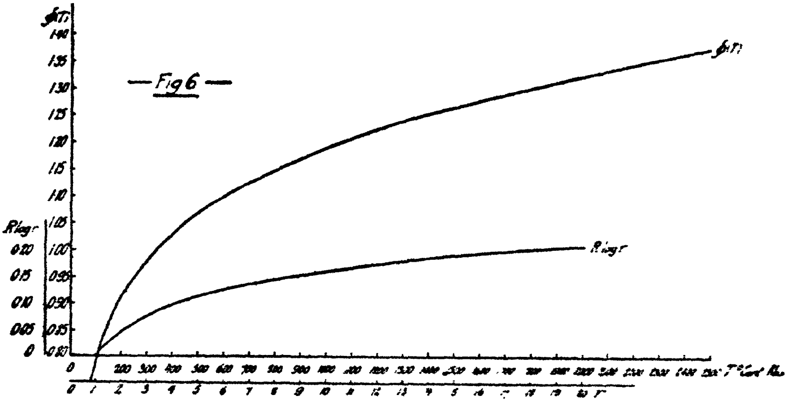
Two diagrams are required, preferably drawn on squared paper. On the first (fig. 6) are plotted values of $\phi(T)$ as ordinates against corresponding values of T as abscissæ. Also on this diagram a curve is plotted giving as ordinates $R \log_e r$ against r as abscissæ.

On the second diagram (fig. 7) are plotted values of $\psi(T)$ as ordinates against corresponding values of T as abscissæ. Also a second curve is plotted to represent $\psi(T) + RT$. To save space, both these curves are shown on the second diagram, instead of having a separate figure for each type of cycle. Accordingly we label these curves respectively I_1, I_2, III_2, IV_1, V_2 and II_1, II_2, III_1, IV_2.

These diagrams may be used in the following manner, and to fix the ideas we shall illustrate their application to cycle I. It is, however, still more convenient to employ fig. 9, as described in paragraph 12.

Suppose T_2, T_3, r to be given. We must find r' by aid of the relations of paragraph 8 for the appropriate cycle. Fig. 6 gives the value of T_1 in terms of T_2 and r in accordance with the adiabatic relation of equation (3). Thus on the axis of abscissæ choose $r=r$, and the ordinate to the appropriate curve represents $R \log_e r$. Choose the value T_2 on the axis of abscissæ, and the corresponding ordinate of the $\phi(T)$ curve gives $\phi(T_2)$. Subtract the ordinate $R \log_e r$ from the ordinate $\phi(T_2)$, and, with this difference as ordinate, proceed horizontally to intersect the $\phi(T)$ curve. This intersection corresponds to T_1. In like manner T_4 is obtained in terms of T_3 and r'.

Fig. 6.



Next we use fig. 7 to give H_3-H_2 and H_4-H_1. Erect ordinates at the positions corresponding to T_2 and T_3 to meet the $\psi(T)$ curve. The difference between the ordinates represents H_3-H_2 to scale.

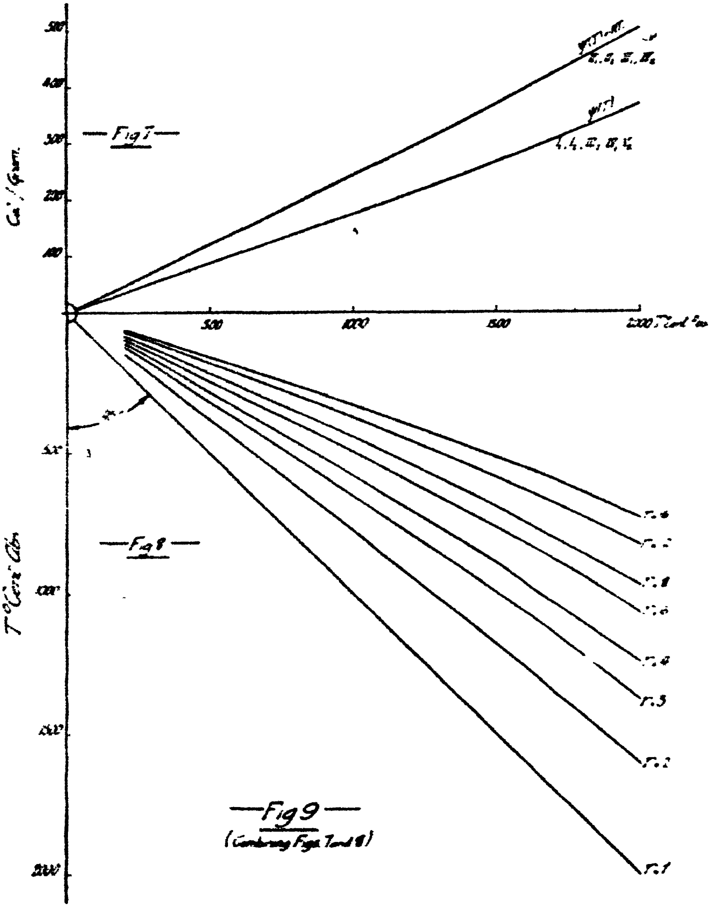
In like manner the difference between the ordinates at T_4 and T_1 to the $\psi(T)$ curve represents H_4-H_1. Thus H_3-H_2 and H_4-H_1 are immediately obtained, and the value

$$\eta=\frac{(H_3-H_2)-(H_4-H_1)}{H_3-H_2} \quad \text{follows.}$$

For cycle II. a few trials may be necessary in finding T_4 from fig. 6. There

$$r' = \frac{rT_2}{T_1T_3}T_4,$$

Fig. 9 (combining figs. 7 and 8).



and we know T_2, T_3, r, and have just determined T_1. Assume a probable value of T_4, and with the resulting value of r' use fig. 6 to find T_4. This will give an indication of the value of T_4, and a further trial value can be chosen and the process repeated until the value of T_4 resulting from fig. 6 agrees with the trial value.

No other difficulties are encountered except with cycle V, where, in finding H_3-H_2, the value of ρ is involved. The appropriate curve may be added to fig. 7, and be labelled V_1 to correspond with the particular value of ρ. Or, instead of obtaining the value of H_3-H_2 wholly from the curve, the part $RT_3\left(1-\frac{1}{\rho}\right)$ may be calculated directly in the expression given in paragraph 9.

11. Where the curves of specific heats cannot well be represented by algebraic formulæ, we may construct ϕ and ψ by a graphical (or tabular) process, thus:—

Plot (or tabulate) the values of C_v against the corresponding values of T. Then at a large number of values of T plot (or tabulate) $\frac{C_v}{T}$. The area between this curve and the axis of abscissæ, and bounded by ordinates at T_1 and T_2, represents approximately the value of

$$\int_{T_1}^{T_2}\frac{C_v}{T}dT.$$

Plot a curve representing at each point T upon it the area measured from $T=0$ to $T=T$. This is the curve $\phi(T)$ of paragraph 6.

In like manner the area contained between the curve C_v and axis of abscissæ, and bounded by the ordinates T_1 and T_2, represents approximately the value of

$$\int_{T_1}^{T_2} C_v\,dT.$$

Plot a curve representing the area measured from $T=0$ to $T=T$. This is the $\psi(T)$ curve of paragraph 7.

12. The construction of fig. 6, by which the adiabatic relation of T and v is determined, may be more conveniently arranged in the form shown in fig. 8. In that figure T′ and T are the coordinates, and the curves marked 1, 2, 3, ... are drawn to correspond with values of $r=1$, $r=2$, etc. Thus to find T_2, corresponding to the value of $r=r$ and $T=T_1$, it is merely necessary to follow the ordinate through T_1 to its intersection with the curve r, and the intercept gives the value of T_2, which is on the same adiabatic with T_1, corresponding to the value r.

Fig. 8 may be prepared with the aid of fig. 6, or may be constructed directly from the equations.

It is convenient to arrange fig. 8 on the same sheet with fig. 7, and the efficiencies may then be obtained very readily (see fig. 9).

In this form the diagram may be most conveniently drawn and employed for calculating the thermal efficiencies of various ideal cycles.

13. The diagram may, however, also be used as a convenient means for determining the values of T, v that lie on the same adiabatic, and also the values that correspond to the same total heat put into the gas. When several sets of values are obtained in this way, they may be plotted on a pressure-volume diagram with the aid of the relation $pv=\mathrm{R}\mathrm{T}$.

In this manner we can draw on the pressure-volume chart the isothermal lines $pv=\mathrm{RT}=\text{constant}$, the adiabatic lines for p, v (since those for T, v have been obtained), and the lines of constant total heat H.

Thus the calculations involved in the preparation of such a chart are facilitated, and information similar to that given in a Mollier chart is obtained.

Such chart may be employed to give the thermal efficiency by plotting on it the given values of T_2, T_3, v_1, v_2 that define the cycle, and completing the diagram with the aid of the adiabatics. When this is done, the total heats put in or taken out may be got from the total heat lines on the chart. Thus H_1, H_2, H_3, and H_4 are obtained, and

$$\eta=\frac{(H_3-H_2)-(H_4-H_1)}{H_3-H_2}$$

is deduced.

14. So far the method has been described in general terms. We have now to obtain suitable numerical values for the constants. For air the values of C_p and C_v are given in tables by Partington and Shilling in calories per gram or C.H.U. per lb.

Examination of these figures indicates that their second differences are small. Accordingly it is found that they can be represented to an accuracy within the probable errors of experiment by the equations

$$C_v=0\cdot1717+5\cdot4\times10^{-6}t+1\cdot09\times10^{-8}\times t^2 \text{ calories per gram,} \quad . \quad . \quad . \quad (10)$$

$$C_p=0\cdot2403+5\cdot4\times10^{-6}t+1\cdot09\times10^{-8}\times t^2 \text{ calories per gram,} \quad . \quad . \quad . \quad (11)$$

$$R=C_p-C_v=\cdot0686 \text{ calories per gram,} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where t represents degrees centigrade.

The values of C_v and C_p calculated from these formulæ are compared in the following table with those tabulated by Partington and Shilling :—

Temp. ° C.	C_v.		C_p.	
	P. & S.	Calcd.	P. & S.	Calcd.
0	·1715	·17170	·2404	·24030
500	·1771	·17712	·2457	·24572
1000	·1881	·18800	·2566	·25660
1500	·2043	·20432	·2729	·27292
2000	·2260	·22610	·2946	·29470

Converting to degrees centigrade absolute, we put

$$T = 273{\cdot}1 + t,$$

and obtain approximately

$$C_v = 0{\cdot}1710 - 5{\cdot}54 \times 10^{-7}T + 1{\cdot}09 \times 10^{-8}T^2 \text{ calories per gram.}$$

Accordingly for air we have

$$a = 0{\cdot}1710, \qquad b = -5{\cdot}54 \times 10^{-7},$$
$$c = 1{\cdot}09 \times 10^{-8}, \qquad R = 0{\cdot}0686.$$

The diagrams of figs. 6 and 7 have been plotted from these figures.

15. As an example of the use of the digrams, we shall find the thermal efficiency of a Diesel cycle using real air, in which it is given that the compression ratio is 14, the ratio of volumes at end and beginning of ignition is 1·75, and the temperature at end of compression is 850° C. abs.

In our notation $T_2 = 850$, $r = 14$, $\rho = 1{\cdot}75$.

From paragraph 8, $T_3 = 1487$, $r' = 8$.

With the aid of the diagram (fig. 9) we commence at the point $T_3 = 1487$ on the axis of abscissæ, and proceed vertically to intersect the $\psi + RT$ curve in the point of which the ordinate is $H_3 = 362$.

On the other side of the axis of abscissæ proceed vertically from $T_3 = 1487$ to the curve $r' = 8$ (from which we note that $T_4 = 690$), then horizontally to the 45° line, then vertically to intersect the ψ curve in the point whose ordinate is $H_4 = 120$.

In like manner proceed vertically from $T_3 = 850$ to intersect the $\psi + RT$ curve in $H_2 = 208$, and then to intersect the curve $r = 14$ (which intersection gives $T_1 = 290$). Then proceed horizontally to the 45° line, then vertically to intersect the ψ curve in the point whose ordinate is $H_1 = 50$.

Then $H_3 - H_2$ is proportional to

$$362 - 208 = 154,$$

and $H_4 - H_1$ is proportional to

$$120 - 50 = 70,$$

so that

$$\eta = \frac{(H_3 - H_2) - (H_4 - H_1)}{H_3 - H_2} = \frac{84}{154} = 0{\cdot}545.$$

16. When the gas used as working fluid suffers dissociation, the determination of the thermal efficiency becomes considerably more complex.

An approximate solution may be obtained by following the methods already described.

When, as is sometimes the case, the energy of dissociation may be regarded approximately as varying with the temperature for a particular cycle, the effect may be represented by assuming an apparent specific heat which varies with the temperature and which includes the true specific heat with an addition representing the dissociation energy.

The calculation of the thermal efficiency then proceeds exactly as before, but with the apparent substituted for the true specific heat.

This hypothesis is often justifiable when it is remembered that the figures for dissociation in many cases are not well ascertained and the effect on engine efficiency is often not considerable.

XLIII. *Two Simple Methods of purifying Radium Emanation.* By William G. Moran, *B.Sc., Dalhousie University, Halifax, Canada* [*].

THE many advantages of using radium in the form of emanation for therapeutic purposes are well known. The types of apparatus hitherto used for purifying and tubing the emanation have been usually so complicated that their use has been restricted to a few large institutions where the amount of radium was great enough to justify the cost of the necessary apparatus and highly trained personnel*. There is undoubted need of an apparatus of low cost and simple operation to permit the wider adoption of the emanation method. In addition, such simplification would be of advantage in physical laboratories where radon is used for research purposes.

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[*] Communicated by Prof. G. W. Henderson.

The emanation, as pumped off from an aqueous solution of radium salt, is mixed with relatively large amounts of hydrogen and oxygen. If the emanation comes in contact with stopcock grease, some CO_2 is also generated. Oxygen is readily removed by ignition with hydrogen, while the CO_2 is taken up by KOH. There always remains, however, an excess of hydrogen, the removal of which constitutes the main difficulty in the purification of the emanation.

In the development of the apparatus described below, many of the usual details and complications have been found to be unnecessary. It is felt that its low cost and ease of operation by relatively unskilled technicians justifies this addition to the already rather long list of published descriptions.

In this apparatus the use of liquid air has been avoided, and the purification is by purely chemical means. Furthermore, it was found unnecessary to remove the water-vapour, so that the usual phosphorus pentoxide is dispensed with. This feature has permitted great simplification of the apparatus. The emanation is pumped from the solution into the simple purifying tube, and from there pushed directly into the fine capillary tube.

Two different methods of purification will be described. In the first a hot filament coated with copper oxide ignites the oxygen with part of the hydrogen and oxidizes the excess hydrogen. The second method employs a spark to ignite the oxygen, while the excess hydrogen passes through the walls of a heated palladium tube into the outside air. In both methods crystalline KOH is used to remove the CO_2.

The apparatus figured on p. 401 has been in use for two years at Victoria General Hospital, Halifax, Canada, with 200 mg. of radium. The concentration attained in routine operation is from 75 millicuries to 125 millicuries per cubic millimetre at a pressure of 25 cm. of mercury. This is ample for all therapeutic and most physical purposes, and is quite comparable with the purification obtained with much more complicated apparatus *.

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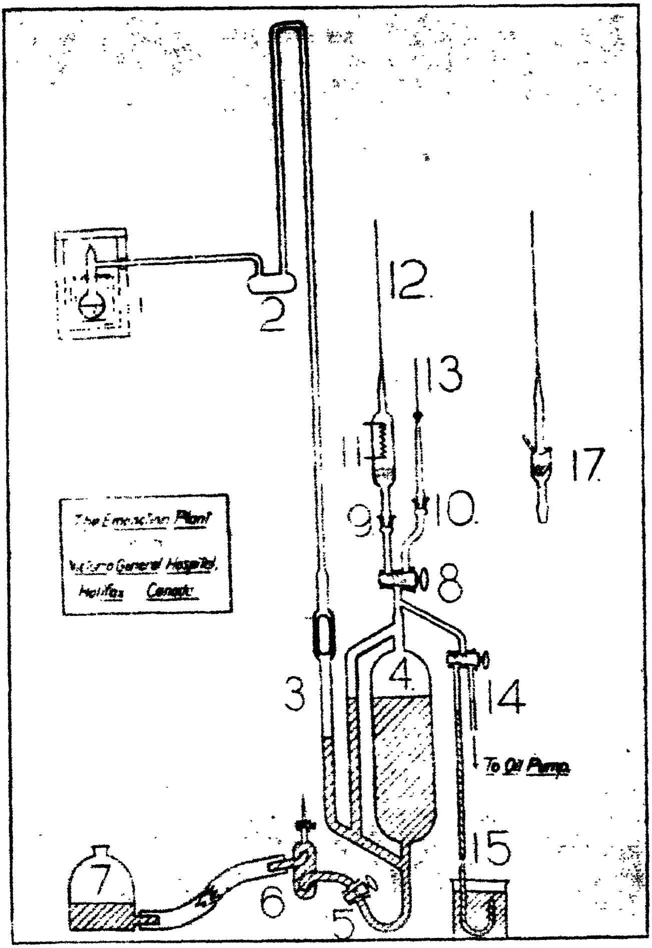
* References to various types of purifying apparatus are given by Hess, Phil. Mag. xlvii. p. 713 (1924). Another type of apparatus has been described by Curtis, J. O. R. S. & R. S. I. xvii. p. 77 (1928).



Method 1.

The radium salt is dissolved in 75 c.c. of water in the flask labelled 1 in the diagram. The emanation and associated gases are withdrawn by the Toepler pump 4, and introduced into the purifying unit 11. The spiral filament shown is of platinum, copper plated and oxidized. When heated electrically to a bright red heat, it readily ignites the oxygen with part of the hydrogen and oxidizes the excess hydrogen. About 10 gms. of KOH fused in a thin layer around the inside wall of the purifying tube removes the CO_2 formed from the lubricant of stopcock 8 and union 9. The purified emanation is then forced up into the thin-walled capillary 12 by lifting the mercury reservoir 7, and is sealed off with a small flame and removed. Most of the water-vapour apparently condenses on the walls as the emanation is forced up into this tube. In the short section containing the purified emanation under a pressure of roughly 25 cm. of mercury, not more than 10 per cent. of the volume can be water-vapour.

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* An earlier emanation plant from which this apparatus was evolved is described by Dr. G. H. Henderson, Trans. N. S. Inst. of Sci. xvii. pt. 1, p. 44 (1926 .

When desired, a portion of the purified emanation may be allowed to diffuse back into the half-emptied pump cylinder 4 and introduced through the other arm of stopcock 8 into the capillary 13. A number of different-sized capillaries mounted on interchangeable male sections of the ground-glass union 10 may be attached, evacuated and filled from a single purification.

The details of the purifying tube are as follows:—The body of the tube is 10 cm. long, 2 cm. diameter. The filament is of platinum wire 20 cm. long, 0·20 mm. diameter, electroplated with copper to 0·35 mm. diameter, and wound into a spiral 5 cm. long. The platinum leads are 0·60 mm. diameter. The filament is heated by a current up to 4 amps. at 8 volts from a small laboratory transformer. The mercury film which adheres to the filament when the mercury is raised up around it is distilled off by a few seconds' heating when the mercury is lowered. The platinum core makes the filament rigid at red heat, so that the usual quartz supporting rod is omitted, while its high melting-point prevents easy burning-out of the filament. Little trouble has been met with from alloying of the platinum and copper. Two such units in constant use for six months are still serviceable. The oxide coating is readily renewed by simply heating in air for a minute. One coating of oxide is sufficient for several hundred millicuries purification. One coating of KOH is sufficient for several thousand millicuries. Quantities as low as 25 m.c. of emanation have been handled, yielding concentrations as mentioned above. Greater concentration is obtained with larger quantities of emanation.

Method 2.

In this method the excess hydrogen passes through the walls of a heated palladium tube into the outside air.

The purifying unit 17 is attached at the interchangeable union 9, in place of unit 11. A palladium tube is sealed through the shoulder of the glass tube as shown. To heat this palladium tube, a current through a few turns of platinum wire 0·20 mm. diameter, wound on a mica sleeve which slips over the tube, is used. The mixture of gases from the solution is introduced into the purifying tube in the same manner as in the previous method. A spark is passed between the inside end of the metal tube, and a platinum wire sealed through the opposite shoulder. This unites the oxygen with the hydrogen. The palladium tube is heated, and the excess hydrogen passes through it into the outside air. Fifteen minutes' heating reduces the inside partial pressure from 1·0 cm. to 10^{-3} mm. of mercury. A layer of KOH removes the CO_2 as in the former method.

The purified emanation is then pushed up into the thin-walled capillary, sealed off under a pressure of about 25 cm. of mercury, and removed; or it may be distributed among various-sized capillaries attached in turn at the interchangeable union 10, and filled as before mentioned. Concentrations as high as 200 millicuries per mm.^{3} have been attained, though 125 millicuries per mm.^{3} is the usual concentration in routine operation. This type of unit is somewhat smaller than the copper-oxide filament type, has nothing to burn out, and gives a slightly higher degree of purification. Five months of steady use has not noticeably lessened the rate of passage of the hydrogen through the palladium.

The details of this unit are as follows:—The body of the tube is 2 cm. long, 2 cm. diameter. The palladium tube is 1·2 cm. long, 2·5 mm. diameter, closed at one end and welded at the other end to a platinum tube of the same diameter, 2·0 cm. long. This welded tube was taken from an old type X-ray tube. The platinum end of the tube is sealed through the glass as shown. A current up to 4 amps. at 8 volts through the wire on the mica sleeve heats the palladium to around 250° C. About 10 gms. of KOH are fused around the inside wall as in the type just described.

The purifying unit is designed so that less than 1 per cent. of the purified emanation is trapped in the palladium tube when the emanation is forced up in the capillary. The mercury film on the inside of the palladium tube is distilled off by a few seconds' heating after the mercury is lowered. No trouble has been met with due to erosion of the metal by the mercury.

It may be mentioned that at any stage in the procedure the emanation may be withdrawn from the purifying tube, pushed out from the delivery tube 15, and collected over mercury in the trough. The use of rubber pressure tubing between the levelling bulb 7 and the Toepler pump 4 has been intentional. It is felt that the use of heavy air-pressures to move mercury in fixed apparatus is attended with very great risks. Attention may also be drawn to the three stopcocks. With the pump cylinder 4 full of mercury and the stopcock turned off, the keys of each in turn may be removed for cleaning, without spilling any mercury or letting air into the apparatus. The last is of some little importance when small quantities of emanation are to be purified. Routine practice has been to clean stopcocks 5 and 14 every six months and 8 every month.

Summary.

A simple apparatus for the purification of radium emanation is described which is low in cost and easy in operation. The use of liquid air is avoided and the removal of water-vapour has been found unnecessary. Two different methods of purification are given. One method ignites the oxygen and hydrogen with a hot copper-oxide filament, which also oxidizes the excess hydrogen. The other method uses a spark to unite the oxygen and hydrogen, while the excess hydrogen passes through the walls of a heated palladium tube into the outside air. The emanation is pumped from the solution into the single small purifying tube. and from there pushed directly up into the thin-walled capillary. The emanation may be withdrawn and collected over mercury at any stage in the purification. The concentration attained compares favourably with the results obtained with the complicated installations.

The author's grateful thanks are due to Dr. G. H. Henderson, Dr. D. MacIntosh, and Dr. H. L. Bronson, of Dalhousie University, for helpful suggestions and appreciated criticism. His thanks are also due to Dr. S. R. Johnston, Radium Therapist, and Mr. W. W. Kenney, Superintendent of the Victoria General Hospital, Halifax, Canada, for their kind and generous support in this research.

XLIV. *On the Waves associated with* β-*Rays, and the Relation between Free Electrons and their Waves.* *By* G. P. Thomson, *M.A., Professor of Natural Philosophy in the University of Aberdeen*[*].

THE following paper is a development of an idea contained in a letter to 'Nature,' published April 21st, 1928, which arose from the work of Ellis and Wooster and others on primary β-rays.

It is now generally accepted that the β-rays of the continuous spectrum are primary products of the disintegration of those radioactive substances which emit them, and that each atom in disintegrating gives one β-ray. This has been shown by Gurney[†] for RaB, RaC, ThB and ThC, and by Emeléus[‡] for RaE. These β-rays cover a wide range of energy (40,000 volts to 1,050,000 volts for RaE), and Ellis and Wooster[§] have shown that the total heating effect of the RaE is represented by the kinetic energy of the β-rays determined from their magnetic spectrum. It follows that this represents the original energy distribution, and that no considerable part of the energy is dissipated either before the ray leaves the atom or in internal changes in the atom after the ray has left it. We are thus reduced to suppose either that the conservation of energy does not apply to each individual process, or that among the atoms either of the RaE or of its product RaF (or both) there are some individuals with a million volts more energy than others, or that there is some way at present unknown by which the atoms can equalize their energies.

It seems difficult to believe that this large amount of energy would not affect previous or subsequent rates of transformation. One might expect, for example, that some atoms of RaF which contained an unusually large amount of energy would break up faster than the rest, so that the curve of decay would not be exponential. Actually, of course, RaF (polonium) was one of the cases from which the exponential law was originally deduced.

The difficulty of supposing that the atoms of RaF as they are formed can arrive at a state of equipartition with one another is greatly increased by the fact that the individual atoms may be widely spaced with non-radioactive atoms in between. Radiation by quanta in the ordinary way would in many cases be absorbed by these neutral atoms, which presumably could not store it in their nuclei, but would absorb it photo-electrically and ultimately turn it into heat, contrary to the experiment.

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[*] Communicated by the Author.

[†] Proc. Roy. Soc. cix. p. 540 (1925), and cxii. p. 380 (1926).

[‡] Proc. Camb. Phil. Soc. xxii. p. 400 (1924).

[§] Proc. Roy. Soc. A, cxvii. p. 109 (1927).

The remaining alternative, that the energy is not conserved in each individual act of emission, does not sound so wild to-day as it would have done before the introduction of quantum mechanics; but one would still feel great diffidence in urging its consideration if it were not that, as I hope to show, it appears as a natural consequence of the wave theory of matter in a way which also explains why β-rays should be exceptional in this respect.

On de Broglie's theory a freely-moving particle is accompanied by waves of length $\lambda = h/p$, where p is the momentum of the particle, and, as is well known, this idea has been fully confirmed by diffraction experiments. In most cases so far considered we are concerned with a large number of particles; for example, a beam of cathode rays. In such a case we represent the beam either, if it is regarded as ideally homogeneous, by a simple sine-wave, or, if it is complex, by some sort of Fourier integral. For example, in the simple case of one dimension under no force, we have, as Darwin* has shown,

$$\psi(x, t) = \int e^{i\frac{2\pi}{h}\left(px - \overline{\frac{p^2}{2m} + mc^2}\, t\right)} \phi(p)\, dp, \quad . \quad . \quad (1)$$

where $\phi(p)$ represents the amplitude of waves at a given value of p. In such a case the wave as a whole represents the whole beam, and there is no assignment of any particular wave to a particular particle.

The initial distribution of particles is translated into a wave function at the beginning of the calculation, and the wave "interpreted" at the end by assuming that the square of the amplitude at any point gives the chance of an electron being found there.

In the case of radioactive emission it is necessary to consider a separate wave for each atom, for the equality of particles emitted and atoms transformed is exact and not statistical. This is shown in the case of α-ray transformations by the simultaneous occurrence of α-ray and recoil tracks in a Wilson chamber, and for all transformations by the change in atomic number according to the Fajans-Soddy law. The form of this wave thus becomes a subject for investigation.

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* Darwin, Proc. Roy. Soc. cxvii. p. 258 (1927). (I have included the intrinsic energy, mc^2, throughout, and the expressions therefore differ slightly from his.)

In the case of the primary β-rays the number of particles as a function of their momentum has been measured for RaE by Ellis, and for RaB and ThB by Gurney. In each case the form in the region investigated is not far from an error function. If we write

$$N\,\delta p = N_0 e^{-\frac{(p-p_0)^2}{d^2}}\,\delta p$$

for the number of particles in a range of momentum p to $p+\delta p$, the following table shows p_0 and d; the other columns we shall need later :—

	$p_0\times10^{17}$.	$d\times10^{17}$.	$\bar{\lambda}\times10^{10}$.	$\sigma\times10^{10}$.	$\bar{\lambda}/\sigma$.	$e^{-\bar{\lambda}/4\sigma^2}$.	$\lambda_0'\times10^{10}$.	$\pi\sigma\times10^{10}$.
RaB ……	2·5	1·3	2·6	·80	3·3	·07	2·1	2·5
ThB ……	1·6	1·0	4·1	1·04	4·0	·02	3·2	3·3
RaE ……	3·4	1·8	1·9	·58	3·3	·07	1·6	1·8

Darwin has shown that for one dimension in force-free space an error distribution in momentum corresponds to a wave whose initial intensity is represented also by a (different) error function. The method can be extended to the case of spherical symmetry which presumably applies here. The wave equation is

$$\frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2\nabla^2\psi = -\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} - mc^2\psi,$$

including the intrinsic energy of the electron. For spherical symmetry

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}.$$

Write $u=\psi\,.\,r$, the wave equation becomes

$$\frac{h}{2\pi i}\frac{\partial u}{\partial t} + mc^2\,.\,u = \frac{h^2}{8\pi^2 m}\frac{\partial^2 u}{\partial r^2}.$$

Following Darwin's method, we take

$$u = \int_{-\infty}^{\infty} e^{i\frac{2\pi}{h}(pr-bt)}\,\phi(p)\,dp,$$

and the equation gives

$$b = p^2/2m + mc^2 \quad \text{and} \quad \psi = u/r.$$

Assume for the initial value of ψ when $t=0$,

$$\psi(r,0)=\frac{1}{r}\exp\left[-\frac{1}{2\sigma^2}(r-r_0)^2+\frac{i2\pi}{h}mv(r-r_0)\right].$$

This gives a finite value for $\int_0^r \psi\psi^* \, dr$, and so is permissible. Then

$$\frac{1}{r}\int_{-\infty}^{\infty} e^{i\frac{2\pi}{h}pr}\phi(p)\,dp$$

$$=\frac{1}{r}\exp\left[-\frac{1}{2\sigma^2}(r-r_0)^2+i\frac{2\pi}{h}mv(r-r_0)\right],$$

when, by inversion of the Fourier integral, we find

$$\phi(p)=\frac{\sigma\sqrt{2\pi}}{h}\exp\left[-\frac{1}{2}\left(\frac{2\pi\sigma}{h}\right)^2(p-mv)^2-i\frac{2\pi}{h}pr_0\right]$$

and

$$\psi(r,t)=\frac{1}{r}\frac{\sigma}{\sqrt{\sigma^2+i\,ht/2\pi m}}$$

$$\exp\left[-\frac{1}{2}\frac{(r-r_0-vt)^2}{\sigma^2+i\,ht/2\pi m}+i\frac{2\pi}{h}mv\left(r-r_0-\tfrac{1}{2}vt-\frac{c^2t}{v}\right)\right]. \quad . \quad . \quad . \quad (2)$$

Thus, corresponding to an initial density

$$\rho=\frac{1}{r^2}e^{-\frac{(r-r_0)^2}{\sigma^2}},$$

the distribution in momentum is given by $\phi(p)$ as

$$N=N_0\exp\left[-\left(\frac{2\pi\sigma}{h}\right)^2(p-mv)^2\right].$$

Thus

$$p_0=mv, \qquad d=h/2\pi\sigma.$$

The mean wave-length $\bar{\lambda}$ is $h/p_0=h/mv$.

If σ is regarded as the "uncertainty of position" and d as the "uncertainty of momentum,"

$$d\sigma=h/2\pi,$$

which is Heissenberg's relation

It will be seen from the figures in the table that the uncertainty of position is of the order of the wave-length, and much greater than the size of the nucleus, which might at first sight have been supposed to determine it.

The above investigation neglects the effect of the attraction of the nucleus. Darwin has shown that for constant acceleration in a straight line the solution can still be written in the form (1) if ϕ is taken as a function ϕ' of p and t such that $| \phi'(p.t) | = | \chi(p-mgt) |$ and $\chi(p)$ is the original $\phi(p)$. Thus the same error law of distribution in momentum holds, but about a new mean value. The same would presumably hold for slowly-varying fields. Now, the whole potential drop outside the radius of the L-orbit (say about $2{\cdot}5 \times 10^{-10}$) is only about 20,000 volts, and it would seem that outside this distance, which is of the order of the mean wave-length, the chief effect of the field would be to produce a small change in the mean momentum; it will therefore be neglected in what follows.

It seems to be more than a coincidence that the ratio of λ/σ only varies over a range of from 3 to 4. The values of $\exp - \lambda^2/4\sigma^2$, given in the last column of the table, show that the amplitude at a distance from the centre of the original group of half a wave-length is always less than a tenth of that in the centre. In the above analysis the amplitude and (imaginary) phase of the wave function correspond to quite separate initial conditions, roughly position and velocity. As Schrödinger[*] has remarked, the complex character of the wave equation is more than a mathematical device, and we are not entitled to separate the solution into real and imaginary parts; a graph, for example, of the real part of the wave would have no significance. He has suggested that we are really dealing with an equation involving fourth-order differential coefficients with respect to the space coordinates, which has been factorized into two complex equations of the second order.

Now, in the case of a disturbance in a physical medium, the displacement is a real function of the coordinates, and can be analysed by Fourier series. If the form of the disturbance is known, we can find an expression for the wave-length for which the Fourier coefficient is a maximum. In our case the natural expression to take for the disturbance is the initial "density"

$$\rho = \frac{1}{r^2} e^{-\frac{(r-r_1)^2}{\sigma^2}} .$$

Unfortunately this involves the unknown r_0; but if r_0/σ is large, the expression approximates to (constant) $e^{-x^2\sigma}$, and the calculation can be made.

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[*] Schrödinger, *Ann. der Phys.* lxxxi. p. 109 (1926).

The result is that the wave-length λ_0, for which the Fourier coefficient is a maximum, is equal to $\pi\sigma$. This λ_0 is not directly comparable with $\bar{\lambda}$, because $\bar{\lambda}$ was found by plotting the number of particles against the *momentum* as abscissa instead of against the *wave-length*. It can easily be shown that if we had plotted against wave-length, the maximum ordinate would have come at

$$\lambda_0' = \frac{2\bar{\lambda}}{1+\sqrt{1+4d^2/p_0^2}}.$$

The table shows the agreement between λ_0' and $\pi\sigma$ or λ_0. In view of the neglect of σ/r_0, it is as good as can be expected, and is strong support for the view that the β-ray is governed by a concentrated disturbance in something that behaves like a physical medium.

It should be noticed that the exponential form for the initial disturbance was chosen largely for mathematical convenience. It is true that it gives the observed distribution in velocity of the rays, but probably any disturbance approximately symmetrical and limited to a region of appropriate size would give a distribution of something like the observed Gaussian form. Thus a short portion of a sine curve abruptly terminated at each end gives a function of the form $\frac{\sin^2 k(\lambda-\lambda_0)}{k^2(\lambda-\lambda_0)^2}$. It is doubtful if the experiments could distinguish between a function of this form and one of Gaussian type if the constants were suitably adjusted.

There is, in fact, some reason to suppose that the actual disturbance is like a heavily-damped sine curve having dis-displacements of both signs. One is tempted to regard the wave of the β-ray as the sound produced by the firing of an atomic gun whose bullet is the electron. Just as the existence in a sound-wave of a compression without a rarefaction is impossible, so it seems possible that here also the disturbance should be of both signs. Of course the analogy must not be pressed too far, for the atomic case differs from the real one in that the atomic bullet is controlled by waves after emission, and travels with them. However, it seemed worth while to test whether waves propagated according to an equation of the type suggested by Schrödinger would behave like sound-waves, where a compression automatically produces a rarefaction, or like waves on a stretched string where a displacement, in one direction only, can be propagated unchanged.

Waves in a Lath.

The equation of waves in a thin lath is

$$\frac{\partial^4\psi}{\partial x^4} = -a^2\frac{\partial^2\psi}{\partial t^2},$$

and so is of the type proposed. I used a strip of veneer 7 metres long, 5 cm. wide, and 1·175 mm. thick. This was hung from the roof by long cords spaced 30 cm. apart and loaded with pieces of lead bent over it at intervals of 10 cm. It gave waves slow enough to be easily followed by the eye. There was considerable dispersion, the shorter waves going faster. However the lath was distorted, the disturbance after a short distance consisted of a complete wave with displacements in both directions. This was true whether the lath was bent by the hands and suddenly released, or disturbed by a blow, either concentrated or spread over a considerable length. The ends of the lath were attached to flexible cotton ropes hanging in loose festoons to diminish the reflexion of the shorter waves, which otherwise, on account of their greater speed, might interfere with the formation of the main wave.

It therefore seems most likely that a primary β-ray at the moment of emission is associated with a short heavily-damped wave like the sound-wave caused by an explosion, and that the spreading of this wave by dispersion causes the variation of speed observed in the rays.

Evidence for Particles.

As stated above, it is possible to find a wave function to represent a stream of particles whose existence is only considered at the end of the experiment when it is necessary to account for the effect actually observed, such as the activation of a grain on a photographic plate, a throw on a Geiger counter, or even, if many electrons are present, the deflexion of an electrometer. The question arises as to how far it is desirable or possible to ascribe an individual existence to the particles before their detection. This point comes up especially in the case of radioactivity, where the particles have sufficient energy to be detectable singly and not merely statistically. Gamow * has recently put forward a theory of α-ray emission which regards the α-ray outside the atom as a continuous, approximately monochromatic, wave whose intensity diminishes exponentially with the time, according to the same law as the radioactive decay of the radioactive substance in bulk. There is a corresponding function for the inside of the nucleus, the two satisfying suitable boundary conditions to ensure continuity. Now, a treatment of this kind meets with two difficulties. The wave from a single atom, or even from a very small speck of radioactive matter, must be supposed extremely feeble, especially for a substance of long life, and the chance of a particle occurring simultaneously at two places outside the atom is extremely remote. But actually such a speck gives rise to Wilson tracks, each of which contains a very large number of drops. This difficulty can theoretically be avoided by regarding the formation of each drop as a separate "experiment." Thus there is a very small chance of the formation of the first drop, which can be calculated from the original wave function. When this is formed, a new wave function must be taken, much greater in amplitude and approximately directed on the line from the radioactive speck, because the formation of the drop shows that a particle was there within certain narrow limits of time and space, and presumably came from the speck. The same thing must be done for each drop of the track. While this view is logically possible, it seems very cumbrous, and even greater difficulties arise in the explanation of Geiger and Bothe's experiments, where the "particles" are quanta.

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* *Zeit. für Phys.* li. p. 204 (1928).

The second type of difficulty, which is especially noticeable in radioactivity, is a one-sidedness in the "interpretation." Consider, for example, an atom of radium in a small enclosure. It is possible, at least in theory, to make it emit light and examine the spectrum. This will not affect the radioactivity in any way. Suppose such an examination is made, say, once a second. Then there will come a time when the spectrum will change to that of emanation, and simultaneously, or approximately so, an α-ray will appear which could be detected by its scintillation.

Now, each observation involves making an "interpretation," *i. e.*, a decision as to the position of the α-particle. When the spectrum is that of radium, the α-particle is supposed in the nucleus; when it is that of emanation, the particle is not in the nucleus, and presumably is outside. But the difficulty is this: as long as the particle is judged *in* the nucleus, there is a constant chance of its being found inside or outside at the next observation; but once it has been found outside, we know from experience that there is no chance of its being afterwards found inside again. What was a question of probability has become a matter of certainty. Something of an irreversible nature has occurred, and the only natural explanation is to suppose a particle actually *moving outwards*, at any rate after it has left the nucleus. Such a particle would be supposed to carry the charge, but not to modify the propagation of the wave.

It may be mentioned in passing that concentration of energy in one direction cannot be expressed by representing the wave as a "pocket" concentrated round a point; such a pocket, at least if finite, will spread and lose its shape.

But there is a difficulty in the above view which comes out particularly strongly in the case of the β-ray, and is another reason why it is necessary to abandon conservation of energy in this case. The conception of a particle in motion is almost meaningless unless it can be supposed to have a definite velocity at a definite time. But a short wave-train is not monochromatic, and each wave-length has its own velocity. Which is the velocity of the particle? In a long train there is a corresponding uncertainty in the position of the particle which may be anywhere in the train. This is, of course, an instance of the Heissenberg uncertainty relation for a free particle expressed in terms of wave mechanics, from which it follows as an immediate consequence. In fact, the speed of a particle can only be found accurately if its waves are nearly monochromatic, and this is only possible if the train is a long one, *i.e.*, if the particle's position is very uncertain. The product of the "uncertainties," suitably measured, is $h/2\pi$.

We can, however, keep both the conception of moving particles and the whole analytical machinery of the wave mechanics (at least for free electrons) if we are prepared to allow the possibility of an electron changing speed in force-free space. This can be seen as follows:—Take the wave equation in the form

$$-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t}=\frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2\Delta\psi+\mathrm{U}\psi,$$

where U is the potential energy and Δ is

$$\sum_s\left(\frac{\partial^2}{\partial x_s^2}+\frac{\partial^2}{\partial y_s^2}+\frac{\partial^2}{\partial z_s^2}\right),$$

where x_s, y_s, z_s are coordinates relating each to one of the s electrons in the system, and U is expressed in terms of these coordinates. Then $\rho=\psi\psi^*=|\psi|^2$ is the density of electricity, *i.e.*, the chance of an electron being at the point in question in the $3s$ dimensional space. Schrödinger (*l.c.*) has shown that the quantity

$$j=-\frac{h}{4\pi i m}(\psi\,\mathrm{grad}\,\psi^*-\psi^*\,\mathrm{grad}\,\psi)$$

obeys the continuity equation

$$\frac{\partial\rho}{\partial t}+\operatorname{div} j=0.$$

Thus the motion is statistically the same as if the electrons moved with velocity $V=j/\rho$; *i.e.*, if a swarm of electrons had actually the density $\psi\psi^*$ at some initial time, and if they moved with the above velocity, $\psi\psi^*$ would represent the density at any subsequent time. When only a few, or one, electrons are present if $\psi\psi^*$ represents the initial chance of one being at a point, if it be supposed to move with the above velocity, $\psi\psi^*$ will always represent the chance of its presence, as can easily be seen by considering a large number of similar systems with the electrons initially in all possible positions.

For $s>1$ the above "velocity" is not in three-dimensional space, and so is of little physical significance. We will return to this case later, and consider now the case of one electron as directly applicable to the β-ray problem. Then

$$V=\frac{h}{2\pi m}\,\mathrm{Im}\,.\{\operatorname{grad}\log\psi\},$$

where ψ is given in our case by (2).

This gives $$V=\frac{t(r-r_0-vt)}{t^2+(\sigma^2 2\pi m/h)^2}+v,$$

and it is thus a function of the time; it is obviously radial. If r is the coordinate of the particle, $V=\frac{dr}{dt}$. Let

$$y=r-vt \quad\text{and}\quad \sigma^2 2\pi m/h=T,$$

then $$\frac{dy}{dt}=\frac{t(y-r_0)}{t^2+T^2},$$

which gives $$r=vt+c\sqrt{t^2+T^2}+r_0.$$

The constant of integration C is determined by the initial conditions. If the value of r for the particle at $t=0$ is $r=r_0+\xi$, then the value at any later time is

$$r=r_0+vt+\xi\sqrt{1+(t/T)^2}.$$

Initially the velocity is v in all cases; it then changes, and when t is large

$$r=r_0+vt+\frac{\xi t}{T},$$

giving a velocity $v+\frac{\xi}{T}$.

T measures the length of the wave-train; if T/ξ is large, the velocity is nearly v at all times.

Looked at from the wave point of view, the initial short group will break up as it goes along, owing to dispersion; and after it has gone a distance very large compared with a wave-length, it will consist of an approximately monochromatic wave of slowly-changing wave-length and amplitude. Any portion forms a nearly monochromatic group; and if the whole wave passes into a magnetic field, as in a β-ray spectrum experiment, each such group will undergo a change of direction appropriate to its wave-length. Such a group approximates to the monochromatic wave

$$\psi = a \exp\left[\frac{2\pi i}{h}\{vx - t(mc^2 + \tfrac{1}{2}mv^2)\}\right],$$

which gives $V = p/m$ as on ordinary mechanics. As is well known, the group velocity in such a case is also p/m, so that the particle keeps with the group.

Conservation of Energy.

The energy given out by the act of emission may regarded as associated either with the wave or the particle, or both. If we suppose that the ordinary expression $\frac{1}{2}mV^2$, which is known to be true for an ordinary electron (*i.e.* one with a long train of waves), holds in our case also, the energy of the particle will in general change after emission, since V changes. The initial velocity v is, however, the same in all cases, and since the wave is also the same, any energy associated with it will be the same. Thus the total energy of emission is a constant, and the energy left in the atom is constant. On this view, the departure from conservation occurs outside the nucleus, and is *essentially associated with the shortness of the wave-train*, as the above expression for v shows clearly; it is therefore only likely to be noticeable when an electron has been very suddenly accelerated, as in the emission of a β-ray from the nucleus.

Since a particle in a group like this is equally likely to gain or lose a given amount of *velocity*, there will be a statistical gain of kinetic energy in the subsequent motion if second-order terms are considered. If we suppose that the wave possesses energy when highly concentrated which it loses on spreading out, the conservation of energy can be kept as a statistical law.

The variable part of the velocity cannot be directly observed because of the uncertainty principle, but it is necessary to assume it to make the scheme logically self-consistent. To some this may seem an objection to the introduction of particles at all, but it seems impossible to work long with any theory without unobservable quantities coming in; for example, in optics—phase and even frequency come under this head. It is, of course, only the *variation* in velocity which is inaccessible to observation; the average speed can be measured by the most direct method imaginable, namely actual timing, as in des Coudres experiment.

Problems involving more than One Electron.

There are two classes of "many-electron" problems. One which can be treated by representing a stream of electrons as a solution of a wave equation with only three variables; the other in which the wave equation itself must involve $3n$ independent variables, as in the case of a complicated atom. The former method is equivalent to ignoring the mutual action between the electrons, or, at most, to representing it by its average effect on the potential. There is no essential difference from the case of one electron. If, indeed, as is commonly done, the initial beam of electrons is represented by a monochromatic wave, this is an idealization even for a single electron; but however the electron was originally produced, and whatever its original wave-train, by the time it has gone even a fraction of a millimetre, there will be a train of an immense number of waves over which the change in wave-length is quite negligible. The assumption of a monochromatic wave is thus justified for all practical purposes; and if there are many electrons, the only difference is an increase in the effective amplitude of the wave, as long as the Coulomb and Ampère forces between the electrons are negligible. Each electron has its own wave system which determines the chance of its being at any assigned place. The assumption of a single wave for the whole beam is merely a convenient way of superposing the essentially independent effects of the separate electrons.

When, however, the importance of the mutual interactions makes it necessary to use a many-dimensioned wave equation, the definition of velocity which we have used so far breaks down. This case occurs especially with the electrons which form part of an atom. In these cases the conception of velocity loses most of its value as there is no practical means of measuring it, even approximately. Schrödinger has shown, however, that it is possible, even in this case, to devise a consistent definition. Thus, if the density associated with electron σ is defined by

$$\rho_\sigma = \int \ldots \int \psi \,.\, \psi^* \, \tau_1 \tau_2 \ldots \tau_{\sigma-1} \,.\, \tau_{\sigma+1} \ldots \tau_N,$$

where the quantities τ_1 etc. are the elements of space associated with the various electrons, and we define a quantity,

$$\iota_s = \int \ldots \int \frac{h}{4\pi i m} (\psi \operatorname{grad} \psi^* - \psi^* \operatorname{grad} \psi) \tau_1 \tau_2 \ldots \tau_{\sigma-1} \tau_{\sigma+1} \ldots \tau_N,$$

then

$$\frac{\partial \rho_\sigma}{\partial t} + \operatorname{div} \iota_s = 0.$$

Thus, if ρ_s is regarded as measuring the probability of the presence of the electron, ι_s/ρ may be taken for its velocity. ‖ I understand from a conversation with Prince L. de Broglie that, in a paper at the last Solvay Conference, he has considered the results of applying his expression for the velocity of a particle (which is practically the same as that used above) to the case of a non-monochromatic wave. See also 'Wave Mechanics,' de Broglie and Brillouin, p. 136 (note in English edition).

Summary.

(1) The variation of the speed of the electrons in the continuous β-ray spectrum can be regarded as due to the dispersion of a short wave-group associated with each ray.

(2) The mean velocity is about that to be expected if the group had the form of an error function of sufficient spread to give the observed range of velocity.

(3) The possibility of a group in the form of a heavily-damped wave is considered, and an experiment described concerning the propagation of waves along a thin lath.

(4) An expression is considered for the velocity of an electron associated with a given wave, and it is shown to give consistent results in this problem. It leads to the consequence that the velocity of an electron may vary even in force-free space, which explains Ellis and Wooster's experiment on the heat generated in the disintegration of RaE. This variation of velocity is essentially associated with a short wave-train.

Aberdeen,
Jan. 7th, 1929.

XLV. *On the Superficial Properties of Mercury.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

M. L. OLIPHANT and L. L. BIRCUMSHAW have published in the September issue of the Philosophical Magazine the results of some researches on the superficial properties of mercury.

M. L. Oliphant states a selective absorption of carbon dioxide by a fresh surface of mercury; L. L. Bircumshaw re-examines the long-debated question of the true value of the surface tension of mercury in vacuum and in various gases. Both the authors come to the conclusion that the variations of surface tension observed in mercury by Stöckle, but not always observed by other physicists, have an effective existence.

Both the authors suggest the hypothesis of a superficial molecular or atomic orientation or arrangement in liquid mercury.

Now, as a matter of fact, some researches I have accomplished in 1921–22 [*] give a direct and strong support to the idea of a superficial atomic or molecular arrangement in mercury. I concluded that "*la surface fraîche du mercure change avec le temps, pour atteindre un arrangement* (*atomique ou moléculaire*) *ayant la plus grande stabilité; c'est à dire ...... la plus petite énergie potentielle de la couche double superficielle, donc la plus petite tension superficielle.*

"Cet arrangement s'achève dans un temps très court (celui dit de *relaxation* ?) dans le vide, mais il est fortement ralenti par les chocs moléculaires du gaz, si la surface de mercure y est préparée. Si la surface est préparée dans le vide, puis qu'on introduise le gaz, les chocs ne sont désormais plus capables de détruire l'arrangement déjà accompli.

"Tout le mond remarquera la relation entre ces idées et les récentes théories de M. Langmuir sur la constitution de la couche superficielle des liquides. Peut-être, dans ce cas, est-on conduit plus directement à l'hypothèse d'un arrangement superficiel d'un liquide."

The experiments were carried on by the large-drop method in different gases (air, CO_2, N_2, H_2) at various pressures (0·1 mm. to 100 mm. Hg): an asymptotical value of the surface tension is reached the more quickly the more rarefied is the surrounding gas.

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[*] *Atti Acc. Torino,* lvii. p. 81 (1921); *id., ib.* lvii. p. 541 (1922). *C. R.* clxxv. p. 519 (1922).

The statement of such a molecular surface rearrangement throws light upon Stöckle's results, and does not disprove the experimental conclusions of M. L. Oliphant. It is likely that molecular arrangement of fresh liquid surfaces can be paralyzed as well by molecular bombardment from the surrounding gas, as by selective absorption.

The very object and the fundamental result of my researches was the close connexion between surface tension and voltaic character *.

Perhaps that is the reason why Mr. Oliphant and Mr. Bircumshaw have passed over the experimental arguments I have pointed out in favour of molecular rearrangement in a fresh surface of mercury.

Believe me,
Yours faithfully,
Prof. ELIGIO PERUCCA

Torino.
16 September, 1928.

XLVI. *Uniformly-diffused Light through Two Apertures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the Philosophical Magazine for November 1928, No. 39 (p. 1019), there is a paper by Mr. L. F. Richardson on "The Amount of Uniformly-diffused Light that will go in Series through Two Apertures forming Opposite Faces of a Cube."

In that paper the author gives an approximate solution of the question by the method of finite differences. He finds that "the amount of light, uniformly diffused with brightness I, that will go in series through two apertures forming opposite faces of a cube of edge l" is

$$\Phi=(0{\cdot}6278\pm 0{\cdot}0001)l^2\mathrm{I}.$$

This case has an accurate solution in the following form †:

$$\Phi=\left(4\sqrt{2}\operatorname{arc\,tg}\frac{1}{\sqrt{2}}-\pi+\lg\frac{4}{3}\right)l^2\mathrm{I}.$$

Yours truly,
A. GERSCHUN.

The Photometr. Laboratory,
State Optic. Institute,
Leningrad.
November 19th, 1928.

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* Intended as the place of the metal in the voltaic series.

† The above-mentioned question can be regarded as a particular case of an example given in R. A. Herman's book, 'A Treatise on Geometrical Optics' (Cambridge, 1900), Chapter ix. Example 16, p. 218.

XLVII. *Notices respecting New Books.*

Collected Physical Papers of Sir Jagadis Chunder Bose. With 123 illustrations. (Longmans, Green & Co., 1927. Price 10*s.* net.)

THIS volume contains a collection of the papers on Physics written by Sir Jagadis Bose. Many of them were written a considerable number of years ago, some of them dating back thirty years or more, to the time when the study of the properties of electric waves, stimulated by Hertz's important experiments, was engaging the attention of a large number of experimental physicists. In these researches Bose played a part by his introduction of a method of generating electrical waves of shorter length than those in general use at that time. He obtained in this way results concerned with polarization, double refraction, and cognate topics which are of importance. It is therefore of value to have available in one volume a reprint of these papers of Sir Jagadis Bose.

The volume contains a number of other papers which are also of interest to the physicist, which trace the gradual building up of his methods for dealing with the properties of living matter. We may therefore recommend the volume, not only to the attention of physicists, but also to all those who are interested in the new aspects of biology which have been studied by Sir Jagadis Bose,—aspects which cannot well fail to be of very considerable importance when the biological sciences come to be further developed in these domains where the recent findings of physics, chemistry, and bio-chemistry are relevant.

Thermodynamics applied to Engineering. By Arthur F. Macconochie, B.Sc. [Pp. xv+260, with 65 figures and two folding charts.] (London: Longmans, Green & Co., Ltd., 1927. Price 12*s.* 6*d.* net.)

The author has divided his treatment of engineering thermodynamics into three sections. The first section contains an elementary treatment of thermodynamical principles with a discussion of various simple cycles, followed by a brief account of the properties of fluids in motion. Section II. deals with the application of these principles to boilers; steam-engines, including the uniflow engine; steam and impulse-reaction turbines. Section III. deals with the application to internal combustion engines, including Diesel engines and gas turbines, and to refrigerating plant. The treatment is elementary throughout, and the volume is intended to meet University degree requirements.

A useful series of tables of thermodynamic properties of saturated steam, superheated steam, saturated ammonia vapour, saturated mercury vapour, and of carbon dioxide, as well as a table of the mean specific heat of superheated steam and tables of trigonometric functions and of logarithms, are added. In a pocket at the end are given Mollier diagrams of total heat and Entropy for steam and of total heat and pressure for ammonia.

A valuable feature for the student is the addition at the end of each section of a list of topics for discussion, a selection of worked numerical examples, and a number of examples for the student. A large proportion of these examples are taken from the examination papers for B.Sc.(Eng.) London.

Vorlesungen über Theoretische Physik an der Universität Leiden. Von Prof. H. A. Lorentz. Band I. *Theorie der Strahlung.* Bearbeitet von Prof. A. D. Fokker. [Pp. x+81, mit 17 Figuren.] (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1927. Price, geb. M.7.80.)

The publication of the lectures on theoretical physics, delivered by the late Prof. Lorentz at the University of Leiden, is proceeding contemporaneously in England and Germany. The first volume of the German edition is devoted to the lectures on the theory of radiation; these are included in the second volume of the English edition. Both are translations from the second Dutch edition, edited by Prof. Fokker.

The lectures, which were delivered in the years 1910–11, are concerned with the classical researches of Kirchhoff, Boltzmann, Wien, and Planck; the last section of the volume deals with the radiation formula of Planck. They are written with the clearness of thought and lucidity of expression which were characteristic of Prof. Lorentz. No attempt has been made to include more recent developments of the theory, but the volume can be recommended as giving one of the best accounts of the classical bases of the theory of radiation. As an elementary introduction to more advanced study it cannot be improved upon.

Wien-Harms, Handbuch der Experimentalphysik: Band XV. "*Radioaktivität,*" von K. W. F. Kohlrausch. [Pp. xii+885 mit 285 Abbildungen.] (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1928. Preis geh. M.79; geb. M.81.)

A brief introduction is followed by three long chapters, devoted respectively to the γ-, β-, and α-rays (treated in this order). These chapters occupy nearly three-fourths of the whole book. Shorter chapters follow, on recoil atoms, miscellaneous effects of the radiations, transformation theory, the experimental technique of Radioactivity, a general account of the radioactive families and their members, and the nucleus of the atom, respectively.

This arrangement of the subject-matter—æsthetically less satisfying than the historical-inductive development of radioactive theory—is, no doubt, in part dictated by the obvious difficulties in the way of any attempt to present a contemporary and comprehensive account of a rapidly expanding experimental science.

The arrangement adopted by Professor Kohlrausch has the merits of facilitating reference to specific problems, and of providing a framework on which newer work can be grafted, in succeeding editions, with a minimum of interference with the existing plan of the book.

The treatment is throughout comprehensive rather than specialized, encyclopædic (generally in the best sense of the term) rather than critical. It is a difficult task for a single writer to cover the whole field of modern radioactivity; it is, therefore, no matter for surprise that Professor Kohlrausch should have been most conspicuously successful in his chapter on γ-ray problems, where he is a recognized authority. Other parts of the field are less completely covered, but the extensive bibliography of original papers, and the excellent Author Index, make the work very useful for reference.

The book is an outstanding example of fine—even luxurious—standards in production. The diagrams are beautifully drawn and very clearly reproduced (although Pettersson's condensation apparatus presents an unfamiliar aspect when printed upside down, with the mercury and liquid air apparently levitating in their respective tubes!). There can be no doubt that the book calls for a genuine tribute to the enterprise of the publishers and to the industry and scholarship of the author. Although its appeal will necessarily be most cogent in Middle European countries, the volume should also find a welcome here.

XLVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. vi. p. 1072.]

November 7th, 1928.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

Dr. L. F. SPATH gave an account of the recent landslide at 'Windy Corner,' above Rocken End, in the Isle of Wight, and referred to some alarming reports that had appeared in the Press. He showed a series of lantern-slides, which, as he suggested, told their own story.

The structure of the Undercliff was simple; it was not unimportant to remember that there was a slight seaward dip, and that porous rocks rested on impervious clays. Landslips were thus bound to recur at more or less frequent intervals. The resisting and curiously weathered chert-beds that form so conspicuous a feature near the top of the cliff, occasionally overhang, but, in spite of being extensively fissured, they do not break away so readily as might be imagined. In July, however, there was a considerable fall; and some views taken while this fall was actually in progress were most impressive. After this fall the débris of Chalk, Chloritic Marl, and 'Upper Greensand' were banked up against the cliff, reaching almost to the top and covering the road below.

After two months the unstable foundation on which this enormous weight had fallen (that is, remains of previous falls and landslips) gave way. On September 21st there was a vast subsidence of the pile of rocks at the top, and a slipping of the whole Undercliff in front of it out to sea. The slide was doubtless helped by the lubricating action of the water thrown out at the junction of the porous rocks above and the Gault clay below (locally known as 'Blue Slipper'). Moreover, the Gault not only formed the foundation (resting on a more solid base of the Sandrock Series), but was present in various isolated masses brought down in former landslips, and all this confused mass was constantly being eroded at the seaward end. The upper portion of the sunken mass with its chasms, leaving a fine, slickensided, cliff-section down almost to the base of the Gault (250 to 300 feet from the top), was particularly impressive. Lower down, there were seen remains of the ashphalt-surface of the destroyed Undercliff road (about 900 feet altogether), pushed down by the rock avalanche, a pond in course of formation, and the heavily fissured ground below as far as Rocken End. This quaking ground of confused material, being forced forward, even pushed up the floor of the sea, and formed a ridge, a little way out, which, however, was rapidly worn away again.

The whole mass was still moving, and small fresh falls occurred during the speaker's visit a few days after the slide; but he appealed to the Fellows to look for ammonites in the Passage-Beds between the Gault and the 'Upper Greensand' as soon as the cliff-section was approachable, perhaps in the spring.

November 21st, 1928.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Geology of the Country around Kenilworth (Warwickshire).' By Frederick William Shotton, B.A., F.G.S.

The paper deals with an area of 59 square miles, of which Kenilworth forms the centre, and completes the mapping of the so-called 'Permian' rocks at the southern termination of the Warwickshire Coalfield. The strata are shown to be conformable with the Carboniferous deposits on the north, and must therefore be regarded as belonging to that system. The total thickness of post-Keele Carboniferous beds is estimated at about 3500 feet, with the top of the sequence overlapped unconformably by Keuper sandstone. Various subdivisions are made, the most important being a well-developed conglomerate (Gibbet Hill Conglomerate) above the Tile Hill Marl Group, and two breccia-bands at Kenilworth. The pebbles of these coarse beds have been examined petrographically, and compared with possible parent-sources (Nuneaton, the Lickey Hills, the Welsh borderland), and from this evidence, and several other lines of inquiry, views have been formulated concerning the geography and earth-movements of the period. The possible relationship of the Kenilworth breccias to those of Clent is also discussed.

The superficial deposits of the area have been mapped for the first time. They are divisible into an eastern and a western type, and subdivisions have been made in each. The eastern deposits show considerable regularity of disposition. A small mammalian fauna is recorded from interglacial gravels, believed to be older than the Chalky Boulder Clay.

Fluvio-glacial gravels and a series of five terraces along the course of the Avon are also dealt with.

2. 'The Carboniferous Section at Cattybrook, near Bristol.' By Stanley Smith, M.A., D.Sc., F.G.S., and Sidney Hugh Reynolds, M.A., Sc.D., F.G.S., Professor of Geology in the University of Bristol.

About 5 miles north of Bristol the Carboniferous Limestone rim of the Bristol Coalfield is traversed by the South Wales branch of the Great Western Railway, by means of the Patchway Tunnel. In the railway-cuttings west of that tunnel, and in the adjacent brickworks, the rocks which are the subject of this paper are exposed. The rocks represented are the uppermost part of the Carboniferous Limestone (D_2 and probably D_1) and the Coal Measures. The D_2 beds, which are mainly calcareous, are finely exposed in the cutting for the down-line, which affords (with the possible exception of the Avon Section) the finest exposure of this horizon in the Bristol district. Red, coarsely oolitic and current-bedded limestones, which often pass rapidly into grits, are the most characteristic rocks. The limestones contain much iron, which often gives to them a characteristically streaky appearance.

At the western end of the main cutting the D_1 beds and Coal Measures are brought into contact by the Cattybrook Fault, and on both sides of this for some 200 yards the rocks show an astonishing amount of disturbance. East of the fault the D_1 beds are traversed by a powerful line of thrust, and every surface hard enough to show this feature is slickensided. West of the fault the ironstone-bands in the Coal Measures may be crumpled up, or torn apart so as to resemble a series of isolated nodules; while the bands of anthracite may be shattered into little bits about a quarter of an inch or half an inch long, or reduced to lenticular pieces 2 to 4 inches long, each bordered by slickensided surfaces.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 1.

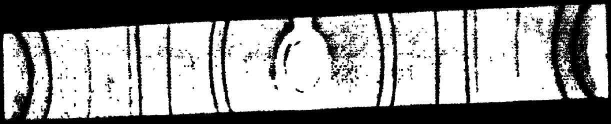


Fig. 2.

Fig. 3.

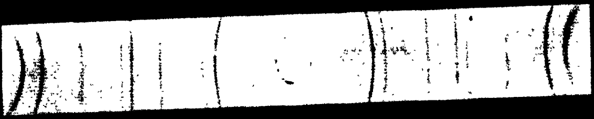


Fig. 4.

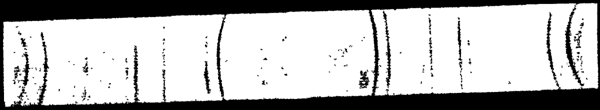


Fig. 5.

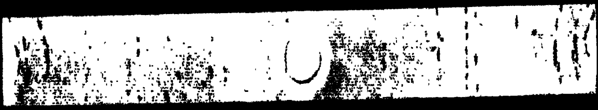
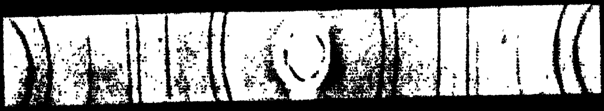


Fig. 6.



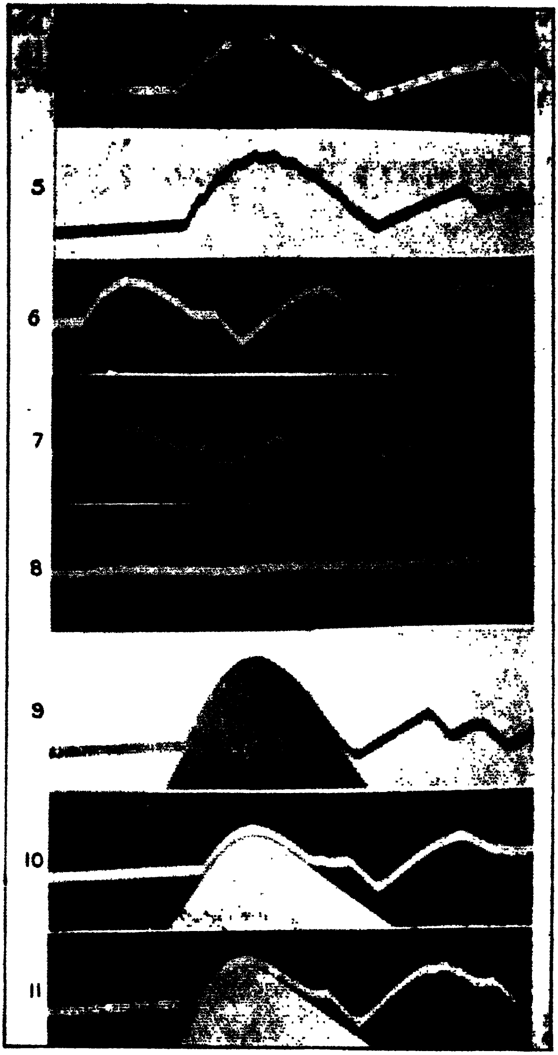

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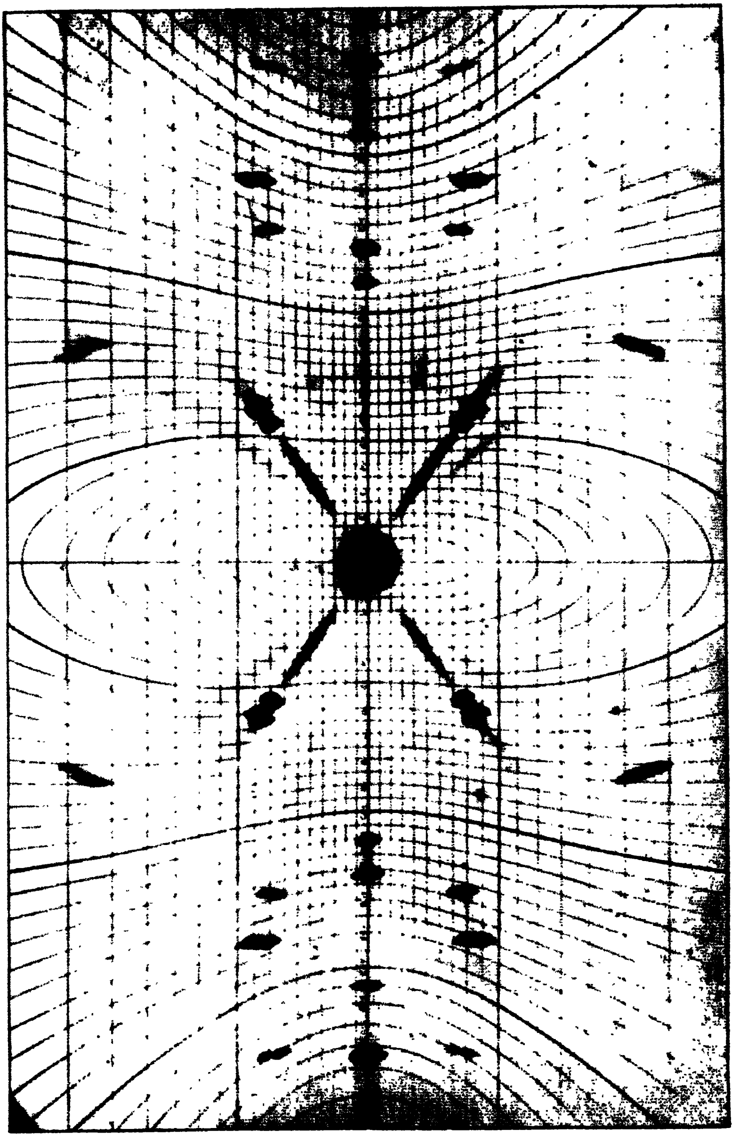
FIG. 3.



Example of appearance of actual X-ray film when the grid method is used in taking a single crystal rotation photograph.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

MARCH 1929.

XLIX. *On the Electromagnetic Field of an Electron.—The Electron as a Gravitational Phenomenon.* *By* D. MEKSYN[*].

§ 1. *The Properties of an Electron and the Special Theory of Relativity.*

ACCORDING to the present Electrodynamics, an Electron is an atom of charge in its own Electromagnetic Field; the latter could be represented as a system of stresses self-balanced in the whole field and resolved into a force acting on the Electron itself.

We make an attempt to discard this picture of an Electron, and we assume that an Electron represents the same entity as a neutral mass, with the only difference that, whereas matter, or energy, is located in a particle in a very small region, in an Electron it is spread all over the space according to the law $\frac{A}{r^4}$, or, what turns out to be the same, that an Electron is a Field of Gravitation whose potential is not $\frac{m}{r}$, but $\frac{m}{r^2}$; there are no stresses in the Field of an Electron[†].

It is true that it is now accepted in some quarters that the stresses have no physical reality, and are only convenient mathematical conceptions. It makes, however, no difference whether we consider them to be real or not, if only we accept the consequences which follow from this conception, as, for instance, the existence of an Electromagnetic Force, the connexion between the mass and Energy etc.

---

[*] Communicated by H. T. Flint, D.Sc.

[†] The Electron is assumed to have a special localization about a point from which r is measured, and the law of extension applies outside this central localization.

The "abolition" of stresses clears up from the outset some of the difficulties connected with the theory of Electrons.

1. If there are no stresses (or the stresses are mathematically equal to zero), an Electron does not possess an Electric Field, and hence it is unnecessary to "explain" the existence of an Electron. An Electron is a substance which is in equilibrium just as a mass particle.

2. From the dynamics of the Theory of Relativity it follows that mass and Energy are connected by

$$m=\frac{W^0}{c^2} \qquad \text{. . . . . (1)}$$

This is, however, not borne out by the Electron Theory, because, according to the latter, the momentum of an Electron is equal [*] to

$$G=\frac{4W^0 u}{3c\sqrt{c^2-u^2}}; \qquad \text{. . . . . . (2)}$$

hence the mass is equal to

$$m=\frac{4W^0}{3c^2} \qquad \text{. . . . . (3)}$$

If, however, we discard the stresses, the momentum will be

$$G=\frac{uW^0}{c\sqrt{c^2-u^2}} \qquad \text{. . . . . . . (4)}$$

and the mass

$$m=\frac{W^0}{c^2}, \qquad \text{. . . . . (5)}$$

or in complete agreement with dynamics.

3. The Law of Energy for an Electron is not satisfied for an accelerated Motion.

If we assume that the mass of an Electron is wholly electromagnetic, its momentum will be

$$G_x=\frac{4W^0 u}{3c^2\sqrt{1-\frac{u^2}{c^2}}}, \qquad \text{. . . . . . (6)}$$

---

[*] M. v. Laue, 'Die Relativitätstheorie,' 1921, p. 134.

and Energy

$$W = \frac{c^2 + \frac{1}{3}u^2}{c^2\sqrt{1 - \frac{u^2}{c^2}}} W^0. \quad . \quad . \quad . \quad (7)$$

The Equation of Energy is

$$u\frac{dG_x}{dt} - \frac{dW}{dt} = \frac{d}{dt}\frac{\sqrt{1 - \frac{u^2}{c^2}}}{3} W^0; \quad . \quad . \quad . \quad (8)$$

or in order to preserve the Law of Energy, it is necessary to admit the existence of some additional mechanical Energy of value [*]:

$$\frac{\sqrt{1 - \frac{u^2}{c^2}}}{3} W^0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In our case this difficulty also disappears because the Momentum and Energy are equal to

$$G = \frac{uW^0}{c^2\sqrt{1 - \frac{u^2}{c^2}}}, \qquad W = \frac{W^0}{\sqrt{1 - \frac{u^2}{c^2}}}, \quad . \quad . \quad (10)$$

and hence the Law of Energy is satisfied.

§ 2. *The Gravitational Field of an Electron.*

1. *Classical Theory.*—According to the classical theory, the Gravitational Potential of continuous matter is given by

$$\nabla^2\phi = -4\pi k\rho, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where ρ is the density of matter and k the constant of Gravitation.

In our case

$$\rho = \frac{e^2}{8\pi c^2 r^4}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

hence

$$\nabla^2\phi = -\frac{ke^2}{2c^2r^4}$$

and

$$\phi = -\frac{ke^2}{4c^2r^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

---

[*] M. v. Laue, *ibid.* p. 226.

2. *The Theory of Relativity.*—The Gravitational potential could be directly obtained from Einstein's solution for Gravitational waves [*].

We give here a somewhat different solution for a particular case in which

$$ds^2 = -(1+2\Omega)(dx^2+dy^2+dz^2)+(1-2\Omega)\,dt^2, \qquad (14)$$

where Ω does not depend upon time.

The Equations of Gravitation are

$$G_{\mu\nu} = -8\pi k(T_{\mu\nu} - \tfrac{1}{2}g_{\mu\nu}T), \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

where $T_{\mu\nu}$ is the Energy tensor and

$$T = g^{\mu\nu}T_{\mu\nu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

Now, neglecting the terms of the order Ω^2, we have

$$G_{\mu\nu} = \tfrac{1}{2}g^{\sigma\rho}\left(\frac{\partial^2 g_{\mu\nu}}{\partial x_\rho \partial x_\sigma} + \frac{\partial^2 g_{\rho\sigma}}{\partial x_\mu \partial x_\nu} - \frac{\partial^2 g_{\mu\sigma}}{\partial x_\rho \partial x_\nu} - \frac{\partial^2 g_{\rho\nu}}{\partial x_\mu \partial x_\sigma}\right), \qquad (17)$$

which for our case become [†]

$$G_{\mu\nu} = \tfrac{1}{2}g^{\sigma\rho}\frac{\partial^2 g_{\mu\nu}}{\partial x_\sigma \partial x_\rho} = -\tfrac{1}{2}\nabla^2 g_{\mu\nu} = \nabla^2\Omega, \quad . \quad . \qquad (18)$$

and the Law of Gravitation is

$$\nabla^2\Omega = -8\pi k(T_{\mu\nu} - \tfrac{1}{2}g_{\mu\nu}T)\,; \quad . \quad . \quad . \qquad (19)$$

in our case all $T_{\mu\nu}=0$ except

$$T_{44} = g_{44}T_4^4 = \frac{e^2}{8\pi r^4 c^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

and

$$T = g_{\mu\nu}T^{\mu\nu} = T_4^4 = \frac{e^2}{8\pi r^4 c^2}. \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

Now the right side of (19) is equal for $\mu=\nu=1, 2, 3$

$$-8\pi k\left(+\frac{1}{2}\,\frac{e^2}{8\pi r^4 c^2}\right) = -\frac{ke^2}{2r^4c^2}, \quad . \quad . \quad . \qquad (22)$$

and for $\mu=\nu=4$

$$-8\pi k\left(\frac{e^2}{8\pi r^4 c^2} - \frac{1}{2}\,\frac{e^2}{8\pi r^4 c^2}\right) = -\frac{1}{2}\,\frac{ke^2}{r^4c^2}, \quad . \qquad (23)$$

or the same as (22).

---

[*] A. Einstein, 'Über Gravitationswellen,' Berlin, Sitzungsberichte, 1918, p. 154.

[†] A. S. Eddington, 'The Mathematical Theory of Relativity,' 1924, p. 102.

Our assumption as to the value of $T_{\mu\nu}$ is consistent with Einstein's Law of Gravitation.

The Equation of Gravitation becomes

$$\nabla^2\Omega = -\frac{1}{2}\frac{ke^2}{r^4c^2}$$

and

$$\Omega = -\frac{ke^2}{4r^2c^2}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

or the same as in the classical theory.

If we compare this solution with Nordström's and Jeffery's [*], we notice an important discrepancy : our solution is only half of Jeffery's, which is equal to

$$\Omega = -\frac{1}{2}\frac{e^2}{r^3}$$

(if allowance is made for the factor $\frac{1}{4\pi}$ in the expression of the Electromagnetic Energy).

This is due to the value of the Energy Tensor $T_{\mu\nu}$, which was taken by Jeffery under the assumption of existence of stresses. We neglect here the ordinary gravitational contribution to $r : \frac{m}{r}$ which arises from the central localization.

§ 3. *Relative and Invariant Mass.*

If we accept Maxwell's stresses, a well-known difficulty arises in the explanation of the mass of an Electron [†].

We have to discriminate between the relative mass T_{44} and the invariant mass $g_{\mu\nu}T^{\mu\nu}$.

Now it appears that the latter, for Maxwell's stresses, is equal to zero, and hence some additional assumption becomes necessary in order to explain the equality of relative and invariant mass for an Electron at rest.

If we discard the stresses, the invariant mass $g_{\mu\nu}T^{\mu\nu}$ becomes equal for an Electron at rest to its relative mass.

§ 4. *Two Electrons in Space and the Electromagnetic Force.*

We have seen that an Electron does not possess an electromagnetic field ; the latter appears only if we have two or more electrons in space, and is wholly due to the increase (or decrease) of energy of space above (or below) the sum of energies of the two Electrons.

[*] A. S. Eddington, *ibid.* p. 185.

[†] *Id. ibid.* p. 183.

To define the laws of the electromagnetic force we must find the energy of two Electrons.

It is clear that, as both energies are spread over the space, some interaction may arise between them.

We know that the gravitational field of two material points and its energy are found (to the first approximation) by superposition of the two fields and their energies. Hence, if we translate the energy of an Electron as an equivalent energy of a gravitational field of matter, we can make some inferences about the laws of an electromagnetic field by applying the same superposition.

This interpretation can be carried out as follows:—

The energy density of an Electron is equal to

$$\left.\begin{aligned} E&=\frac{e^2}{8\pi r^4}=\frac{1}{8\pi}\left[\left(\frac{\partial V}{\partial x}\right)^2+\left(\frac{\partial V}{\partial y}\right)^2+\left(\frac{\partial V}{\partial z}\right)^2\right], \\ \text{where}\quad V&=\frac{e}{r}. \end{aligned}\right\} \qquad (25)$$

By Green's transformation we have

$$\iiint V\nabla^2 V\,dx\,dy\,dz+\iiint\left\{\left(\frac{\partial V}{\partial x}\right)^2+\left(\frac{\partial V}{\partial y}\right)^2+\left(\frac{\partial V}{\partial z}\right)^2\right\} \times dx\,dy\,dz+\iint V\frac{dV}{dn}\,dS=0. \qquad (26)$$

The last term vanishes at the boundary, and as $V=\frac{e}{r}$, the first term is equal to

$$\iiint V\nabla^2 V\,dx\,dy\,dz=-4\pi\iiint V\rho\,dx\,dy\,dz=-4\pi eV, \qquad (27)$$

whence

$$E=\tfrac{1}{2}eV. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

Hence we come to the conclusion that the energy of an Electron is equal to the energy of a mass e in a gravitational field V, or, from (25), the energy at every point of the field is proportional to the square of its equivalent gravitational Force.

The latter is what we usually call the Electrostatic force of an Electron.

Now, if we have two Electrons to which we ascribe electric forces

$$X_1,\ Y_1,\ Z_1, \qquad X_2,\ Y_2,\ Z_2,$$

the resultant force will be, according to the theory of gravitation,

$$X_1+X_2, \qquad Y_1+Y_2, \qquad Z_1+Z_2,$$

and their common energy

$$\frac{1}{8\pi}\iiint[(X_1+X_2)^2+(Y_1+Y_2)^2+(Z_1+Z_2)^2]\,dx\,dy\,dz$$

$$=\frac{1}{8\pi}\iiint(X_1^2+Y_1^2+Z_1^2)\,dx\,dy\,dz$$

$$+\frac{1}{4\pi}\iiint(X_1X_2+Y_1Y_2+Z_1Z_2)\,dx\,dy\,dz$$

$$+\frac{1}{8\pi}\iiint(X_2^2+Y_2^2+Z_2^2)\,dx\,dy\,dz. \quad . \quad . \quad . \quad . \quad . \quad (29)$$

In (29) the first and the last term represent the energies of the two Electrons, and the middle term the energy of their interaction.

Of this energy

$$W=\frac{1}{4\pi}\iiint(X_1X_2+Y_1Y_2+Z_1Z_2)\,dx\,dy\,dz \quad . \quad (30)$$

is due the so-called ponderomotive force of the field. If $W=0$, there is no mechanical action between two such Electrons.

The derivation of (29) cannot be considered as rigorous. We take the expression of W as one which has to be confirmed *a posteriori* rather than found by deduction.

For the general case of two electromagnetic fields we assume that the extra energy is, as in the case of two electrostatic fields, equal to the scalar product of the six vectors of force, *i. e.*

$$W=\iiint[(X_1X_2+Y_1Y_2+Z_1Z_2)-(\alpha_1\alpha_2+\beta_1\beta_2+\gamma_1\gamma_2)]$$
$$\times\,dy\,dx\,dz \quad . \quad . \quad . \quad (31)$$

where XYZ, $\alpha\beta\gamma$ are the electric and magnetic forces.

§ 5. *An Electron in an Electrostatic Field.*

The extra energy is

$$W=\frac{1}{4\pi}\iiint\left(\frac{\partial V_1}{\partial x}\frac{\partial V_2}{\partial x}+\frac{\partial V_1}{\partial y}\frac{\partial V_2}{\partial y}+\frac{\partial V_1}{\partial z}\frac{\partial V_2}{\partial z}\right)dx\,dy\,dz,$$

or integrating by parts and omitting the surface integral,

$$W=-\frac{1}{4\pi}\iiint V_2\nabla^2V_1\,dx\,dy\,dz=e_1V_2.$$

§ 6. *An Electron in a Magnetic Field.*

The extra energy W (31) vanishes identically (because every term is equal to 0) ; hence there is no mechanical interaction between an electrostatic and magnetostatic field.

§ 7. *An Electron in Motion in an Electromagnetic Field (two Electromagnetic Fields).*

The energy integral is equal to

$$W=\frac{1}{4\pi}\iiint\left[(X_1X_2+Y_1Y_2+Z_1Z_2)-(\alpha_1\alpha_2+\beta_1\beta_2+\gamma_1\gamma_2)\right] \times dx\,dy\,dz.$$

We express the Electromagnetic force by means of a vector and scalar potential, and obtain :

$$\begin{aligned} W=\frac{1}{4\pi}\iiint\Big\{\Big[\Big(-\frac{\partial\psi_1}{\partial x}-\frac{\partial F_1}{\partial t}\Big)&-\frac{\partial\psi_2}{\partial x}-\frac{\partial F_2}{\partial t}\Big) \\ &+\Big(-\frac{\partial\psi_1}{\partial y}-\frac{\partial G_1}{\partial t}\Big)\Big(-\frac{\partial\psi_2}{\partial y}-\frac{\partial G_2}{\partial t}\Big) \\ &+\Big(-\frac{\partial\psi_1}{\partial z}-\frac{\partial H_1}{\partial t}\Big)\Big(-\frac{\partial\psi_2}{\partial z}-\frac{\partial H_2}{\partial t}\Big)\Big] \\ &-\Big[\Big(\frac{\partial H_1}{\partial y}-\frac{\partial G_1}{\partial z}\Big)\Big(\frac{\partial H_2}{\partial y}-\frac{\partial G_2}{\partial z}\Big) \\ &+\Big(\frac{\partial F_1}{\partial z}-\frac{\partial H_1}{\partial x}\Big)\Big(\frac{\partial F_2}{\partial z}-\frac{\partial H_2}{\partial x}\Big) \\ &+\Big(\frac{\partial G_1}{\partial x}-\frac{\partial F_1}{\partial y}\Big)\Big(\frac{\partial G_2}{\partial x}-\frac{\partial F_2}{\partial y}\Big)\Big]\Big\}dx\,dy\,dz. \quad . \quad . \quad (32) \end{aligned}$$

We integrate (32) by parts, and obtain a volume integral :

$$\begin{aligned} W_1=-\frac{1}{4\pi}\iiint\Big\{\psi_2\Big[&\frac{\partial^2\psi_1}{\partial x^2}+\frac{\partial^2\psi_1}{\partial y^2}+\frac{\partial^2 G_1}{\partial t\partial y}+\frac{\partial^2\psi_1}{\partial t^2}+\frac{\partial^2 H_1}{\partial t\partial z}+\frac{\partial^2 F_1}{\partial t\partial x}\Big] \\ &+F_2\Big[\frac{\partial^2\psi_1}{\partial x\partial t}+\frac{\partial^2 F_1}{\partial t^2}-\frac{\partial^2 F_1}{\partial z^2}+\frac{\partial^2 H_1}{\partial x\partial z}+\frac{\partial^2 G_1}{\partial x\partial y}-\frac{\partial^2 F_1}{\partial y^2}\Big] \\ &+G_2\Big[\frac{\partial^2\psi_1}{\partial y\partial t}+\frac{\partial^2 G_1}{\partial t^2}+\frac{\partial^2 H_1}{\partial y\partial z}-\frac{\partial^2 G_1}{\partial z^2}-\frac{\partial^2 G_1}{\partial x^2}+\frac{\partial^2 F_1}{\partial y\partial x}\Big] \\ &+H_2\Big[\frac{\partial^2\psi_1}{\partial z\partial t}+\frac{\partial^2 H_1}{\partial t_2}-\frac{\partial^2 H_1}{\partial y^2}+\frac{\partial^2 G_1}{\partial z\partial y}+\frac{\partial^2 F_1}{\partial z\partial x}-\frac{\partial^2 H_1}{\partial x^2}\Big]\Big\} \\ &\times dx\,dy\,dz. \end{aligned}$$

Making use of the equation :

$$\frac{\partial F_1}{\partial x}+\frac{\partial G_1}{\partial y}+\frac{\partial H_1}{\partial z}+\frac{\partial \psi_1}{\partial t}=0,$$

we obtain

$$W_1=-\frac{1}{4\pi}\iiint\Big\{\psi_2\Big(\nabla^2\psi_1-\frac{\partial^2\psi_1}{\partial t_2}\Big)+F_2\Big(\frac{\partial^2 F_1}{\partial t^2}-\nabla^2 F_1\Big)$$

$$+G_2\Big(\frac{\partial^2 G_1}{\partial t^2}-\nabla^2 G_1\Big)+H_2\Big(\frac{\partial^2 H_1}{\partial t_2}-\nabla^2 H_1\Big)\Big\}dx\,dy\,dz.$$

From the electron theory we have

$$\nabla^2\psi_1-\frac{\partial^2\psi_1}{\partial t^2}=-4\pi\rho_1,$$

$$\nabla^2 F_1-\frac{\partial^2 F_1}{\partial t^2}=-4\pi\rho_1\frac{u}{c};$$

. . . .

hence

$$W_1=\iiint\rho_1\Big(\psi_2-\frac{uF_2}{c}-\frac{vG_2}{c}-\frac{wH_2}{c}\Big)dx\,dy\,dz$$

$$=e_1\Big(\psi_2-\frac{uF_2}{c}-\frac{vG_2}{c}-\frac{wH_2}{c}\Big). \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

This is the expression used for the potential energy in Lagrange's equations, and is obtained from Lorentz's electromagnetic force.

The remaining parts of W are

$$W_2=-\frac{1}{4\pi}\iiint\Big[\frac{\partial}{\partial x}(\psi_2X_1+G_2\gamma_1-H_2\beta_2)$$

$$+\frac{\partial}{\partial y}(\psi_2Y_1-F_2\gamma_1+H_2\alpha_1)$$

$$+\frac{\partial}{\partial z}(\psi_2Z_1+F_2\beta_1-G_2\alpha_1)\Big]dx\,dy\,dz$$

$$-\frac{1}{4\pi}\iiint\frac{\partial}{\partial t}(F_2X_1+G_2Y_1+H_2Z_1)\,dx\,dy\,dz.$$

The first integral is a surface one, and vanishes if the expressions in brackets are of the order of $\frac{1}{r^3}$.

The last integral is a volume one, and it represents some additional energy not accounted for by Lorentz's Force.

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L. *Dr. A. N. Whitehead's Theory of Absolute Acceleration.*

By WILLIAM BAND, *B.Sc., George Holt Physics Laboratory, Liverpool University* *.

Foreword.

THIS communication criticizes the fundamental assumption involved in Dr. A. N. Whitehead's Theory of Relativity, as contrasted with Einstein's. It also points out a previously unnoticed practical consequence of the theory that is in violent contradiction with fact, quite apart from gravitational and electrical problems.

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1. *Introductory.—The Problem Reviewed.*

ACCORDING to the Special Theory of Relativity, space and time are united in a single space-time continuum, and any particular division of this continuum into space and time is not merely a property of the continuum, but of the relation of the continuum as a whole to the observer who makes the division. There is no such thing as *the* history of events; there is a history for every observer, the same only when the observers are in relative rest, but different when they are in relative uniform rectilinear motion. Einstein was able in his general theory to give mathematical expression to the natural generalization that all observers are equally competent to erect a coordinate system even when in relative acceleration, no observer being singled out as unaccelerated in any absolute sense. The differences between the coordinate systems erected by any two observers will depend entirely on their relative motion, and everything we could know about the latter we could deduce from the former.

Whitehead's theory is a natural reaction to this generalized theory. He accepts the verdict of the Special Relativity, that when two observers are in relative uniform rectilinear motion they will erect different coordinate systems even when momentarily at the same position (1). But he rejects, in effect, the generalization that observers in relative acceleration, but momentarily at relative rest, will also construct differing coordinate systems. According to Dr. Whitehead, an accelerated observer A will pass continually through the various uniform velocities, and his coordinate system will be identical at any instant with that of an unaccelerated observer momentarily at rest relative to A at the instant in question(2). The observer A is accelerated in an absolute sense(3).

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* Communicated by Prof. J. Rice, M.A.

For brevity we shall adopt the usual convention, and consider as one group the coordinate systems used by all the observers who are only in uniform rectilinear relative velocity, and call this group the consentient set of coordinate systems.

Whitehead's theory states that there is only one consentient set, and that even accelerated observers use it(2). Einstein, on the other hand, supposes that there are an infinity of different sets, none of which can be singled out as corresponding in any absolute sense to unaccelerated observers.

2. *Philosophical Considerations.*

It would appear that, as Professor C. D. Broad has pointed out(4), Whitehead's theory suffers from the same drawbacks as did Newton's. The absolute basis for the measurement of acceleration will in practice be as difficult to find as was Newton's postulated basis for the measurement of uniform motion. Were our knowledge confined to one stellar universe, the Galaxy would serve well enough as a standard for rotation ; but knowing as we do of other stellar universes with rotations relative to our own, we have no right to single out any one as being in any sense absolutely non-rotating. In fact, Whitehead and Newton both require that there should be a single agglomeration, finite in extent, of matter, surrounded by an infinite spread of empty space, both from the above and other (mathematical) considerations(5).

Whitehead's theory has, however, been improved in this respect by Temple's generalization, showing that the isotropic manifold can be adopted(6). The world can then be considered finite, and the total number of stellar universes also finite, so that an average could conceivably be made and adopted as a standard for rotation. While this averaging seems highly artificial, it would appear to be sufficient to raise Whitehead's theory on to a more satisfactory level than Newton's, and it seems to be logically complete, and more or less philosophically sound.

But this last statement is considerably modified by the following considerations.

Whitehead gave the following philosophical justification for Minkowski's unification of space and time(7).

If the instantaneous view of nature contains all the significant factors thereof, motion is merely the visible effect of a sequence of minute changes of position; the coordinates used by an observer in motion would therefore be at any moment identical with those used by an observer at rest at the same point. But if it requires a finite time to exhibit the essential factors of nature, *i. e.* if we can in practice be aware of only finite events, and never limit our sense experience to instantaneous views of nature[(8)], we shall always be able to tell that two bodies have a relative motion even while they appear to be in the same position. The motion of a point is therefore a real factor of nature quite apart from position, and just as essential as position in determining its relations with the world as a whole. We may therefore expect quite reasonably that a relative velocity between two observers will be accompanied by a disparity between the coordinate systems used by them; for the coordinates depend on the observer's relation with the world in general.

But is it logical after this to suppose that a relative acceleration cannot cause a further disparity? If the finite time exhibits velocity as an essential factor apart from position, it will also exhibit acceleration apart from velocity, and the higher derivatives as well. But in this case we are forced to the standpoint of general relativity, that the coordinate system contains all the details pertaining to the motion of the origin, and that no origin can be singled out as unaccelerated.

It thus appears that, when driven to its logical conclusion, the philosophy employed by Whitehead to justify the special relativity will justify the general also, and so nullify his own theory of absolute acceleration.

3. *Practical Consequences.*

Suppose, for the sake of further argument, that we can in fact identify the one consentient set postulated by Whitehead. Let us examine the practical consequences of supposing that the coordinates are independent of the field in which the observer is situated, and let the origin be, moreover, accelerated.

A planet is revolving absolutely about the Sun; there is an observer S at rest on the planet, who constructs coordinates (*s*), correct for a non-rotating planet. Imagine another observer A, permanently at rest in that member of the consentient set in which the planet, neglecting rotation, is momentarily at rest at any given instant, say T. Let A construct the coordinate system (*a*), one of the consentient set. Then the assumption we are examining evidently means that at the instant T, the system (*s*) is momentarily identical in all respects with the system (*a*).

Imagine, now, another observer B at rest in the other member of the consentient set in which the planet is momentarily at rest, say, half a year later at the instant T′. Then at T′ the system (*s*) is in every respect identical with the system (*b*) of the observer B.

But since the observers A and B are moving in opposite directions, the momentary spread of space at T for A will intersect that at T′ for B[9], the region of intersection being an instantaneous plane perpendicular[10] to the line bisecting the arc of the planet's orbit that has been traced between the instants T and T′, and in a direction remote from the Sun. The distance of this plane will, of course, depend upon the particular planet chosen.

Fig. 1

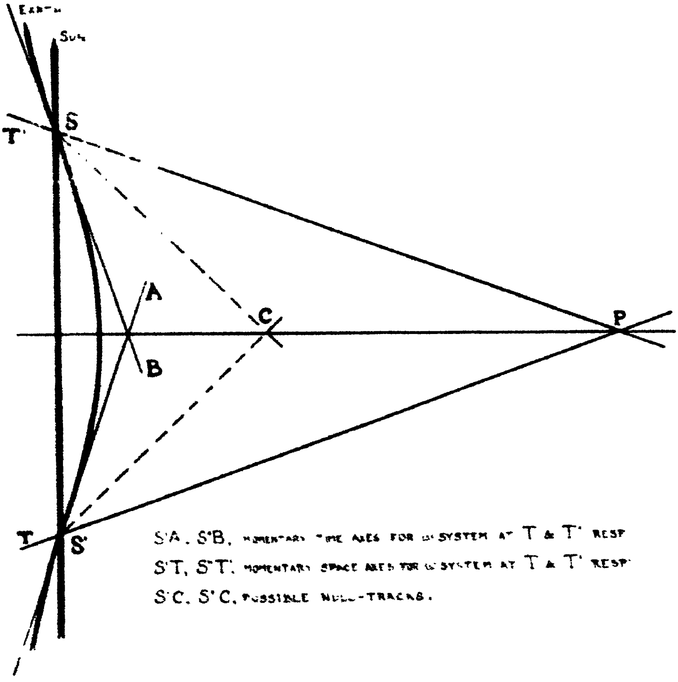
EARTH
SUN
S
T′
A
B
C
P
T
S′
S′A, S′B, MOMENTARY TIME AXES FOR (s) SYSTEM AT T & T′ RESP
S′T, S′T′, MOMENTARY SPACE AXES FOR (s) SYSTEM AT T & T′ RESP
S′C, S′C, POSSIBLE NULL-TRACKS.

Fig. 1 is simplified by including only one space dimension. It is constructed from Minkowski's principles, and shows the intersection of moments or space spreads that are separated by half the year at the origin. We wish to investigate the intersection of moments that are separated at the origin by a vanishingly short time.

Let the planet traverse a short arc PQ which we may treat as circular. The velocity of the planet, relative to the Sun, will have been reversed in a direction parallel to that radius of the orbit which bisects the arc PQ; the radius SX in fig. 2.

Fig. 2.

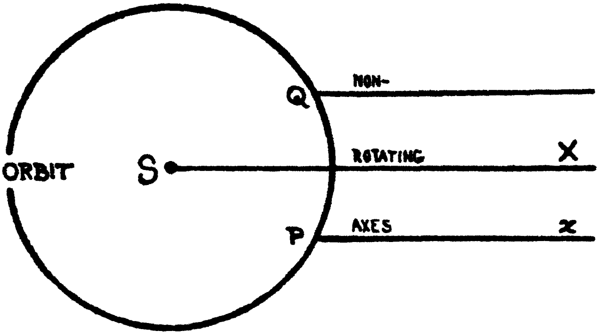

Fig. 3.

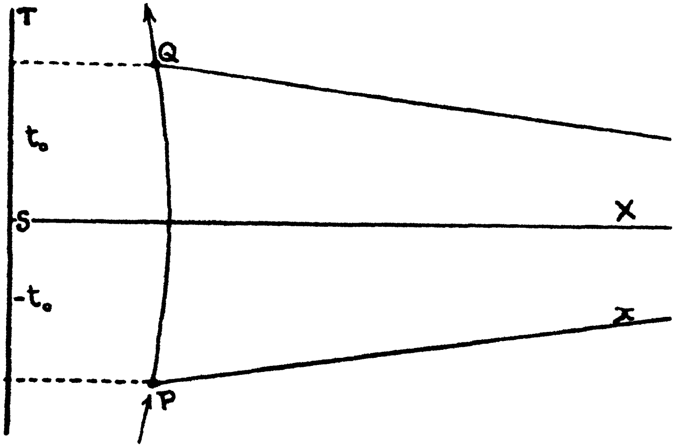

Fig. 2 is a timeless section in the plane of the orbit; fig. 3 is a projection on to a plane containing time and one space dimension. ST is the track of the Sun.

For the purposes of analysis take ST as the t-axis, and SX as the x-axis; the unit of "t" $3 . 10^{-10}$ seconds, and of "x" 1 cm.

The equation of the projection PQ in 3 will be

$$x = a \cos nt,$$

where a is the radius of the orbit, and

$$n = 2\pi/[\text{period of orbit}] = 2\pi/\mathrm{T}, \text{ say.}$$

This gives

$$dx/dt = -an \sin nt.$$

Let Px be the space axis of the planetary observer at P; its gradient in the diagram will be

$$dt/dx = an \sin nt_0,$$

and it passes through the point $(a \cos nt_0, -t_0)$. Its equation will therefore be

$$(t + t_0)/(x - a \cos nt_0) = an \sin nt_0.$$

Its intersection with the axis SX will then be given by putting t zero, *i.e.*

$$x = a \cos nt_0 + t_0/(an \sin nt_0),$$

which is independent of the sign of t_0.

The space axes, or moments, for the observer at P and Q therefore respectively intersect at a distance from the Sun given by this last equation. The distance from the planet will thus be

$$x - a \cos nt_0 = \left[\frac{1}{an^2}\right] [nt_0/\sin nt_0].$$

In the limit when P and Q coincide, or t_0 approaches zero, this reduces to

$$1/an^2 = \mathrm{T}^2/4\pi^2 a$$

in a direction remote from the Sun.

Remembering the units used, we work this out as somewhat less than 10^{20} cm. in this particular case, when the planet chosen is the Earth.

We can interpret this result only by supposing that there is some kind of vagrant horizon always on the side of the planet remote from the Sun. Successive moments close up towards this, and spread out in opposite directions. We should expect that during a total eclipse the stars revealed near the Sun's disk would exhibit a spectral shift to the blue, the shift increasing with the distance of the star; the stars in the opposite ecliptic region would show a spectral shift to the red. The horizon is at the distance of 10^{20} cm.

Eddington⁽¹⁰⁾ gives the distance of the further star clusters as about 10^{21} cm., while the distance of the first magnitude star Arcturus is known to be $1{\cdot}6 \,.\, 10^{20}$ cm. Temple's generalization will merely superpose a general shift to the red, and bring the apparent horizon nearer.

If the horizon is at 10^{20} cm., we require a recessional motion of about $1{\cdot}3 \,.\, 10^{8}$ cm. per sec. at a distance of 4·3 light-years—that of α Centauri, the nearest star to our solar system: this corresponds to a spectral shift relative to terrestrial sources, roughly equal to 40 times the separation between the two Na lines!

4. *Conclusion.*

The assumption that an accelerated observer uses at any moment a member of the consentient set of coordinate systems leads to a curious inconsistency with fact. Had Whitehead been thoroughly reactionary, and been content with Newtonian space independent of an absolute time, the moments for oppositely-moving observers would not have intersected, and the inconsistency would not have arisen. The fault lies in the attempt to compromise between the idea of absolute acceleration and that of relativity of velocity, for which, as we saw in § 2, the logical justification was doubtful.

By a reversion to a Ptolemaic system of astronomy, Whitehead might be able to explain the above results, but in that case his mathematical ingenuity would be taxed with the problem of discovering a dynamic invariant that would account for the revolution of the Sun about the Earth—not a particularly hopeful proposition.

References.

(1) Whitehead, 'The Principle of Relativity,' p. 88, "Conclusion."
(2) *Loc. cit.* p. 76.
(3) *Loc. cit.* p. 72; 'The Physical Field,' p. 88, "Rotation."
(4) 'Mind,' April 1923; Review of Whitehead, *l. c.*, in "Critical Notices."
(5) Einstein.
(6) Proc. Phys. Soc. London, April 1924.
(7) Whitehead, 'Principles of Natural Knowledge' (?).
(8) On this point see also C. D. Broad, 'Scientific Thought,' pp. 346 *ff*.
(9) Whitehead, *l. c.* § 47.1.
(10) Eddington, 'The Mathematical Theory of Relativity,' § 69, § 102.

LI. *The Aberration Effect on Straight-line Reproduction.*
By ARNOLD BUXTON, *M A. Oxon.*[*]

THE theory of the reproduction of luminous points and lines in a symmetrical optical system depends upon diffraction and the aberration residuals in the system[†].

Hamilton has shown, in his 'Theory of Systems of Rays,' that the time V taken by the light to travel from the point P in the object space to Q in the image space can be expressed as a function of the coordinates of P and Q with respect to certain axes not necessarily the same.

Clerk Maxwell, in his 'Collected Papers,' vol. ii., takes the axis of symmetry of the optical system as one axis (in our case the axis of x), and takes P in a plane through the object-origin perpendicular to the axis of symmetry, and similarly for Q in the image space. He then shows that V may now be regarded as a function of four coordinates Y, Z, η, ζ, since the other two are zero, and then from the symmetry of the optical system about the axis of x the number of variables may be reduced to three. Y^2+Z^2, $\eta^2+\zeta^2$, $Y\eta+Z\zeta$.

Further, if the first and last media of the system have refractive indices unity, then it is a property of V, the characteristic function of Hamilton that

$$\frac{\partial V}{\partial \eta}=M_1, \qquad \frac{\partial V}{\partial \zeta}=N_1, \qquad \frac{\partial V}{\partial Y}=M, \qquad \frac{\partial V}{\partial Z}=N,$$

where L, M, N ; L_1, M_1, N_1 are the direction cosines of the incident and emergent rays respectively, *i. e.*

$$V=F(Y^2+Z^2,\ \zeta^2+\eta^2,\ Y\eta+Z\zeta).$$

Expanding V and rejecting third and higher powers of the new variables, we have

$$\begin{aligned} V = {} & a_0+a_1(Y^2+Z^2)+a_2(\zeta^2+\eta^2)+a_3(Y\eta+Z\zeta)+a_4(Y^2+Z^2)^2 \\ & +a_5(\zeta^2+\eta^2)^2+a_6(Y\eta+Z\zeta)^2+a_7(Y^2+Z^2)(\zeta^2+\eta^2) \\ & +a_8(Y^2+Z^2)(Y\eta+Z\zeta)+a_9(\zeta^2+\eta^2)(Y\eta+Z\zeta)\ \ddagger, \end{aligned}$$

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[*] Communicated by the Author.

[†] A. Buxton, Monthly Notices R. A. S. lxxxi. No. 8, p. 547 (June 1921); lxxxiii. No. 8, p. 475 (June 1923); lxxxv. No. 1, p. 78 (Nov. 1924).

[‡] Clerk Maxwell, 'Collected Papers,' ii. p. 442 (18).

with

$$\begin{aligned}M_1=\frac{\partial V}{\partial\eta}=&\ 2a_2\eta+a_3Y+2\eta a_5(\zeta^2+\eta^2)+2a_6Y(Y\eta+Z\zeta)\\&+2a_7\eta(Y^2+Z^2)+a_8Y(Y^2+Z^2)+2a_9\eta(Y\eta+Z\zeta)\\&+a_9Y(\zeta^2+\eta^2),\quad\ldots\ldots\quad(1)\end{aligned}$$

$$\begin{aligned}N_1=\frac{\partial V}{\partial\zeta}=&\ 2a_2\zeta+a_3Z+2a_5\zeta(\zeta^2+\eta^2)+2a_6Z(Y\eta+Z\zeta)\\&+2a_7\zeta(Y^2+Z^2)+a_8Z(Y^2+Z^2)+2a_9\zeta(Y\eta+Z\zeta)\\&+a_9Z(\zeta^2+\eta^2),\quad\ldots\ldots\quad(2)\end{aligned}$$

and

$$L_1=\sqrt{1-M_1^2-N_1^2}.\quad\ldots\ldots\quad(3)$$

Let X′, Y′, Z′ be the coordinates of the point where the emergent ray meets the image plane, then

$$Y'=\eta+\frac{M_1}{L_1}X',$$

$$Z'=\zeta+\frac{N_1}{L_1}X'$$

from the straight-line equation

$$\frac{x-\xi}{L_1}=\frac{y-\eta}{M_1}=\frac{z-\zeta}{N_1}$$

for the emerging ray. We must now substitute for $\frac{M_1}{L_1}$ and $\frac{N_1}{L_1}$ from (1), (2), and (3)

$$\begin{aligned}\frac{M_1}{L_1}=\frac{M_1}{\sqrt{1-M_1^2-N_1^2}}&=M_1\{1+\tfrac{1}{2}(M_1^2+N_1^2)\}\\&=M_1+\tfrac{1}{2}M_1^3+\tfrac{1}{2}M_1N_1^2\end{aligned}$$

and

$$\frac{N_1}{L_1}=N_1+\tfrac{1}{2}M_1^2N_1+\tfrac{1}{2}N_1^3,$$

i. e.

$$\begin{aligned}\frac{M_1}{L_1}=&\ 2a_2\eta+a_3Y+2\eta a_5(\zeta^2+\eta^2)+2a_6Y(Y\eta+Z\zeta)\\&+2a_7\eta(Y^2+Z^2)+a_8Y(Y^2+Z^2)+2a_9\eta(Y\eta+Z\zeta)\\&+a_9Y(\zeta^2+\eta^2)\\&+\tfrac{1}{2}[a_3^3Y^3+6a_3^2Y^2a_2\eta+12a_3a_2^2Y\eta^2+8a_2^3\eta^3+8a_2^3\eta\zeta^2\\&\quad+8a_2^2a_3\zeta\eta Z+2a_2a_3^2\eta Z^2+4a_2^2a_3Y\zeta^2+4a_2a_3^2YZ\zeta\\&\quad+a_3^3YZ^2]\end{aligned}$$

$$
\begin{aligned}
&= 2a_2\eta + a_3 Y + \eta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) \\
&\quad + 2Y^2\eta(a_6 + a_7 + \tfrac{3}{2}a_2a_3^2) + Y\eta^2(3a_9 + 6a_3a_2^2) \\
&\quad + Y\zeta^2(a_9 + 2a_3a_2^2) + Y^3\left(\frac{a_3^3}{2} + a_8\right),
\end{aligned}
$$

introducing the simplification obtained by making OP the axis of Y or $Z=0$.

Similarly,

$$
\begin{aligned}
\frac{N_1}{L_1} &= 2a_2\zeta + 2a_5\zeta(\zeta^2 + \eta^2) + 2a_7\zeta Y^2 + 2a_9 Y\zeta\eta \\
&\quad + \tfrac{1}{2}[8a_2^3\zeta^3 + 8a_2^3\zeta\eta^2 + 2a_2a_3^2Y^2\zeta + 8a_2^2a_3\zeta\eta Y] \\
&= 2a_2\zeta + \zeta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) + (2a_7 + a_2a_3^2)Y^2\zeta \\
&\quad + (2a_9 + 4a_2^2a_3)Y\zeta\eta.
\end{aligned}
$$

Hence

$$
\begin{aligned}
Y' = \eta + X'\Big[&2a_2\eta + a_3Y + \eta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) \\
&+ 2Y^2\eta(a_6 + a_7 + \tfrac{3}{2}a_2a_3^2) + Y\eta^2(3a_9 + 6a_3a_2^2) \\
&+ Y\zeta^2(a_9 + 2a_3a_2^2) + Y^3\left(\frac{a_3^3}{2} + a_8\right)\Big],
\end{aligned}
$$

$$
\begin{aligned}
Z' = \zeta + X'[&2a_2\zeta + \zeta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) + (2a_7 + a_2a_3^2)Y^2\zeta \\
&+ (2a_9 + 4a_2^2a_3)Y\zeta\eta],
\end{aligned}
$$

or

$$Y' = \eta(1 + 2a_2X') + a_3X'Y + \ldots$$

and

$$Z' = \zeta(1 + 2a_2X') + \ldots.$$

From these results it is evident that, if $1 + 2a_nX' = 0$, neglecting third-order terms, Y' will be proportional to Y and Z' will be zero. Hence $X' = -\frac{1}{2a_2}$ gives the position of the first-order image plane, and the third-order aberrations are given by the equations :

$$
\begin{aligned}
\delta Y' = -\frac{1}{2a_2}\Big[&\eta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) + 2Y^2\eta(a_6 + a_7 + \tfrac{3}{2}a_2a_3^2) \\
&+ Y\eta^2(3a_9 + 6a_3a_2^2) + Y\zeta^2(a_9 + 2a_3a_2^2) \\
&+ Y^3\left(\frac{a_3^3}{2} + a_8\right)\Big], \quad \ldots\ldots\ldots \quad (4)
\end{aligned}
$$

$$
\begin{aligned}
\delta Z' = -\frac{1}{2a_2}[&\zeta(\zeta^2 + \eta^2)(2a_5 + 4a_2^3) + (2a_7 + a_2a_3^2)Y^2\zeta \\
&+ (2a_9 + 4a_2^2a_3)Y\zeta\eta]. \quad \ldots\ldots\ldots \quad (5)
\end{aligned}
$$

II. *The Separate Effects of the Aberrations on the Luminous Line Integrals* *.

(a) *Distortion.*

For distortion, assuming the other aberrations absent,

$$\delta Y' = -\frac{\frac{a_3^2}{2}+a_8}{2a_2}Y^3,$$

$$\delta Z' = 0.$$

This aberration depends only on Y, and is independent of the coordinates η, ζ of the exit pupil. Consequently, the coordinates of the image point are the same for all rays proceeding from the object point. In the absence of diffraction and complete correction of all aberration residuals except distortion, we have, to the degree of approximation contemplated, reproduction of point for point, except that the points in the image will be distorted radially from the axis, according to the law given above.

Taking into account diffraction, the patterns from self-luminous object point, in the presence of distortion only, will again consist, as in the Airy disk, of central concentration of light surrounded by rings of rapidly diminishing intensity. The position of the central concentration will, of course, depend on the distortion present, but otherwise the light-distribution will be the same as for the aberrationless disk. In the case of the luminous straight line, however, the locus of the central concentrations will be a curve representing the distorted image of the straight line due to the presence of distortion in the system.

Taking the case of the luminous line

$$Y = c,$$

$$X = 0.$$

the reproduction, which should have been Q_1M, becomes the curve $Q_1'T$, defined by the relation $Q_1Q_1' = kO_2Q_1^3$ for positive distortion, where O_2 is the point on the symmetrical axis and the image plane.

The coordinates of Q_1' are

$$Y = O_2M + kr^3\cos\theta,$$

$$Z = MQ_1 + kr^3\sin\theta.$$

---

* Lord Rayleigh, "Wave Theory," Encyc. Britannica 9th ed. p. 433.

Taking $O_2M = y$ and $MQ_1 = z$,

$$Y = y + kr^2y = y + ky(y^2+z^2),$$

$$Z = z + kzr^2 = z + kz(y^2+z^2),$$

i. e.

$$\frac{Y}{y} = \frac{Z}{z},$$

and the equation of the curve $Q_1{}'T$ is

$$Y^2(Y-y-ky^3) = ky^3Z^2,$$

where $y = O_2M$ and constant for the given line.

In like manner the reproduction of $X=0$, $Z=c$ can be determined; the coordinates of $Q_1{}'$ are now

$$Y = y + kr^2y,$$

$$Z = z_1 + kr^2z_1 - kz_1{}^3,$$

giving as the locus of (Y, Z)

$$Z^2(Z-z_1) = kY^2z_1{}^3,$$

where z_1 is the height of the reproduction of the point on the Z-axis, which does not suffer distortion since $Y=0$ for this point. The intensities of light in the reproduction of the first line will be given on the extension of the Airy theory. Thus the intensity at $(Y_1\,Z_1)$ will be given by the following integral*:

$$\int_{s=-\infty}^{s=\infty}\left[\int_{r=0}^{r=1} J_0\left(\frac{r}{f}\sqrt{(Y_1-Y)^2+(Z_1-Z)^2}\right)\pi\,dr^2\right]^2 ds,$$

where (Y, Z) satisfies the equation of the curve

$$Y^2(Y-y-ky^3) = ky^3Z^2,$$

and ds is an element of arc at that point. The above formula guides us as to the distribution of light in the distorted diffraction pattern due to the reproduction of the first luminous line, and will consist of a band parallel to the central reproduction along the curve in fig. 1. The corresponding integral for the second curve in fig. 2 will be the same except that (Y, Z) will satisfy the equation

$$Z^2(Z-z_1) = kY^2z_1{}^3.$$

---

* 'Proceedings of the Optical Convention, 1926,' pt. 2, p. 771. [The ratio of semi-aperture to focal length is taken as of the order $\frac{1}{30}$ throughout.]

The diffraction band will again be parallel to and symmetrical about its central curve in fig. 2.

Similarly, the distorted curves could be obtained for other straight lines in the image space, and the corresponding diffraction bands investigated.

Fig. 1.

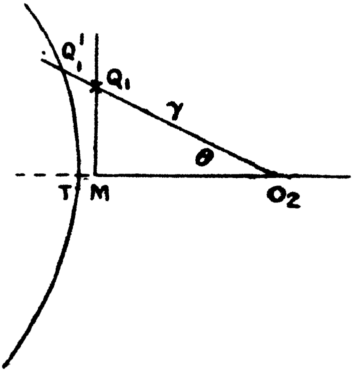
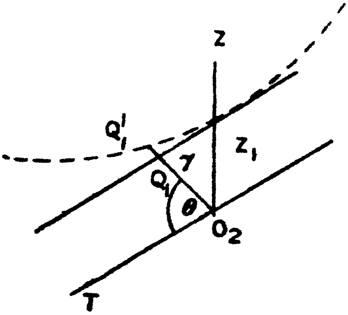


Fig. 2.



(b) *Spherical Aberration.*

Assuming all other aberrations absent except spherical aberration, we have, from equations (4) and (5),

$$\delta Y' = -\frac{1}{2a_2}\eta(\zeta^2+\eta^2)(2a_6+4a_2^3),$$

$$\delta Z' = -\frac{1}{2a_2}\zeta(\zeta^2+\eta^2)(2a_6+4a_2^3),$$

so that

$$\frac{\delta Y'}{\eta} = \frac{\delta Z'}{\zeta}.$$

These expressions indicate that the spherical aberration is independent of Y, and that a ray from a point on the axis in the image space is brought to a focus at a point where

$$X' = -\frac{1}{2a_2} + \alpha,$$

where

$$\frac{\alpha}{X'+\alpha} = \frac{\delta Z}{\zeta} = \frac{\delta Y}{\eta} = -\frac{a_5 + 2a_2^3}{a_2}(\zeta^2 + \eta^2) = -k_2 r^2.$$

Hence α, the longitudinal spherical aberration, can be expanded as a series of even powers of the aperture, verifying a result which has previously been used in determining the distribution of light in the diffraction patterns of a luminous point source in the presence of spherical aberration *. Regarding the luminous line as built up of luminous points, we have, on integration,

$$\left[\int_{-\infty}^{+\infty}\left[\int_0^1 J_0\left(\frac{r\sqrt{Y'^2+Z'^2}}{f}\right)\cos c_2 r^4 \pi \, dr^2\right]^2 dZ'\right]$$
$$+\int_{-\infty}\left[\int_0^1 J_0\left(\frac{r\sqrt{Y'^2+Z'^2}}{f}\right)\sin c_2 r^4 \pi \, dr^2\right]^2 dZ',$$

as representing the value of the intensity at (Y′Z′) in the diffraction pattern of a luminous line in the presence of spherical aberration due to a circular aperture.

(c) *Curvature and Astigmatism* are included in the terms:

$$\delta Y' = -\frac{1}{2a_2}\{a_6 + a_7 + \tfrac{3}{2}a_2 a_3^2\} 2Y^2\eta,$$

$$\delta Z' = -\frac{1}{2a_2}\{a_7 + \tfrac{1}{2}a_2 a_3^2\} 2Y^2\zeta,$$

and coma in the remaining terms:

$$\delta Y' = -\frac{1}{2a_2}(3\eta^2 + \zeta^2)(a_9 + 2a_3 a_2^2)Y,$$

$$\delta Z' = -\frac{1}{2a_2}\{2\eta\zeta(a_9 + 2a_3 a_2^2)\}.$$

---

* Monthly Notices, R. A. S. lxxxi. No. 8, p. 554.

The curvature and astigmatism residuals may be written as

$$\frac{\delta Y'}{Y^2} = -\eta(3k+k_1),$$

$$\text{where } k = a_3^2 - \frac{a_6}{a_2},$$

and

$$\frac{\partial Z'}{Y^2} = -\zeta(k+k_1),$$

$$\text{and} \quad k_1 = \frac{a_6 - 2a_7}{2a_2}.$$

If $k=0$, then, in the first-order image plane, we have

$$\delta Y' = -k_1 Y^2 \eta,$$

$$\delta Z' = -k_1 Y^2 \zeta,$$

and as the extreme rays of the pencil satisfy $\zeta^2+\eta^2=r^2$, we have

$$(\delta Y')^2 + (\delta Z')^2 = k_1^2 Y^4 r^2,$$

giving a circle about the Gaussian image point, the radius of which increases as Y increases. Hence there is again a point image situated off the ideal image plane at a distance from it which is different for different object points except for the point of the object which lies on the axis with its $Y=0$. Thus the image of a flat object takes the form of a curved surface of revolution which touches the ideal image plane at its vertex. k_1 is therefore a measure of the curvature of the field:

$$\frac{\delta Y'}{\eta} = -Y^2(3k+k_1),$$

$$\frac{\partial Z'}{\zeta} = -Y^2(k+k_1),$$

i. e.

$$\frac{(\delta Y')^2}{(3k+k_1)^2} + \frac{(\delta Z')^2}{(k+k_1)^2} = r^2 Y^4,$$

giving an ellipse about the Gaussian point as centre when $k \neq 0$; when $k_1=0$, one axis is three times the other. At the point (h, k) farther along the emergent ray and on the plane parallel to and distant α from the ideal focus plane, we have the line joining (η, ζ) and $(Y'+\delta Y', Z'+\delta Z')$ divided externally in the ratio $\frac{\alpha}{X'+\alpha}$,

i. e.

$$X'h = (X'+\alpha)(Y'+\delta Y') - \alpha\eta,$$

$$X'k = (X'+\alpha)(Z'+\delta Z') - \alpha\zeta$$

or
$$X'h = (X'+\alpha)\left[-\frac{a_3}{2a_2}Y - Y^2\eta(3k+k_1)\right] - \alpha\eta,$$
$$X'k = (X'+\alpha)\left[-Y^2\zeta(k+k_1)\right] - \alpha\zeta,$$
i. e.
$$X'h + (X'+\alpha)\frac{a_3 Y}{2a_2} = -\eta\left[\alpha + Y^2(X'+\alpha)(3k+k_1)\right],$$
$$X'k = -\zeta\left[(X'+\alpha)(Y^2)(k+k_1)+\alpha\right],$$
i. e.
$$\zeta^2+\eta^2 = \frac{\left(X'h + \frac{(X'+\alpha)a_3Y}{2a_2}\right)^2}{\{\alpha+Y^2(X'+\alpha)(3k+k_1)\}^2} + \frac{X'^2k^2}{\{Y^2(X'+\alpha)(k+k_1)+\alpha\}^2} = r^2.$$

There are two special cases of this ellipse :

(*a*) when $\alpha + Y^2(X'+\alpha)(3k+k_1) = 0$,

(*b*) „ $\alpha + Y^2(X'+\alpha)(k+k_1) = 0$.

(*a*) gives
$$\alpha(1+3kY^2+k_1Y^2) = \frac{Y^2}{2a_2}(3k+k_1),$$
i. e. $$\alpha = \frac{Y^2}{2a_2}(3k+k_1) \quad \text{approx.}$$

(*b*) gives, similarly,
$$\alpha = \frac{Y^2}{2a_2}(k+k_1).$$

For these two cases the ellipses reduce to straight lines :

(*a*) parallel to the Z-axis,

(*b*) „ „ „ Y-axis,

and are known as the focal lines. If k_1 is zero, we see at once that the tangential focal line is three times the distance of the sagittal focal line from the first-order image plane, which now takes the place of the Petzval surface of revolution. When k_1 is not zero, the ray intersects—

the Petzval surface where $\alpha = \frac{Y^2}{2a_2}k_1$,

the sagittal focal line where $\alpha = \frac{Y^2}{2a_2}(k+k_1)$,

and the tangential focal line where $\alpha = \frac{Y^2}{2a_2}(3k+k_1)$.

The theorem is then still true, that within third-order approximation the tangential focal line is three times the distance of the sagittal line from the surface of Petzval. For the value of α equal to $\frac{1}{2}\frac{Y^2}{2a_2}[3k+k_1+k+k_1]$ the axes of the ellipse of section of the pencil are now equal, so that midway between the tangential and focal lines we have the circle of least confusion. The distribution of light in the images of a self-luminous point in the presence of astigmation and curvature of the field have been dealt with for a flat field in the Monthly Notices, R. A. S., and the results can be extended in the usual way by integration to include the luminous line under the same conditions. The integrals for the intensities in the different image planes become very unwieldy, and are not amenable to ready calculation.

(d) *Coma.*

Lastly, in the presence of coma we have, as was indicated,

$$\delta Y' = -\frac{1}{2a_2}(3\eta^2+\zeta^2)Y(a_9+2a_3a_2^2),$$

$$\delta Z' = -\frac{1}{2a_2}(a_9+2a_2^2a_3)2\eta\zeta . Y.$$

Writing $\eta = r\cos\theta$,

$\zeta = r\sin\theta$, and the common constant equal to k,

$$\left.\begin{aligned}\frac{\delta Y'}{kY} &= r^2(2+\cos 2\theta),\\ \frac{\delta Z'}{kY} &= r^2\sin 2\theta,\end{aligned}\right\}\text{ giving }\left(\frac{\delta Y'}{kY}-2r^2\right)^2+\left(\frac{\delta Z'}{kY}\right)^2=r^4,$$

defining the coma patch in the Gaussian plane.

This patch is seen to consist of a series of circles with centres $(2r^2kY, 0)$ and radii kr^2Y, giving the well-known shape of the coma figure enclosed between two lines at 60°. The square root of the intensity in the central concentration along the Y′ axis can be shown to be proportional to the integral

$$\int_0^1 J_0(\mu r+\mu_1 r^3)\pi\, dr^2,$$

where μ and μ_1 are constants. The corresponding intensity at any point near the coma axis can be written in the form:

$$I = C^2 + S^2,$$

where C is proportional to

$$\int_0^1 \int_0^{2\pi} \cos\{\mu r \cos(\phi - \alpha) - \mu_1 r^3 \sin\phi\}\, d\phi\, r dr,$$

$$\text{with} \quad \alpha = \tan^{-1}\frac{\delta Y'}{\delta Z'},$$

and S proportional to

$$\int_0^1 \int_0^{2\pi} \sin\{\mu r \cos(\phi - \alpha) - \mu_1 r^3 \sin\phi\}\, d\phi\, r dr,$$

Writing $\psi = \phi - \alpha$,

$$C = k \int_0^1 \int_0^{2\pi} \cos\{\mu r \cos\psi - \mu_1 r^3 \sin(\psi + \alpha)\}\, d\psi\, r dr$$

$$= k \int_0^1 \int_0^{2\pi} \{\cos(\mu r \cos\psi) \cos[\mu_1 r^3 \sin(\psi + \alpha)]$$
$$+ \sin(\mu r \cos\psi) \sin[\mu_1 r^3 \sin(\psi + \alpha)]\}\, r dr\, d\psi$$

$$= k \int_0^1 \int_0^{2\pi} \Big\{ \cos(\mu r \cos\psi)\left[1 - \frac{\mu_1{}^2 r^6 \sin^2 \psi \mp \alpha}{2} \ldots\right]$$
$$+ \sin(\mu r \cos\psi)[\mu_1 r^3 \sin\psi \cos\alpha + \mu_1 r^3 \cos\psi \sin\alpha + \ldots]$$
$$r dr\, d\psi \Big\}$$

$$= k \int_0^1 \left\{ \frac{2\pi}{\mu} J_0 + \mu_1 \sin\alpha r^3 . 2\pi J_1 \right\} r dr$$

$$\text{since} \quad \int_0^{2\pi} \sin(\mu r \cos\psi) \sin\psi\, d\psi = 0,$$

$$\int_0^{2\pi} \sin(\mu r \cos\psi) \cos\psi\, d\psi = 2\pi J_1$$

$$= k\, 2\pi \left[\frac{J_1}{\mu} + \mu_1 \sin\alpha \int r^4 J_1\, dr\right]$$

$$= k\, 2\pi \left[\frac{J_1}{\mu} + \frac{\mu_1}{\mu} \sin\alpha \left(J_2 - \frac{2J_3}{\mu}\right)\right]$$

$$= \frac{2\pi k}{\mu}\left[J_1 + \mu_1 \sin\alpha \left(J_2 - \frac{2J_3}{\mu}\right)\right].$$

Similarly,

$$S = k\int_0^1\int_0^{2\pi} \sin\{\mu r\cos\psi - \mu_1 r^3 \sin(\psi+\alpha)\}\, d\psi\, r dr$$

$$= k\int_0^1\int_0^{2\pi} \{\sin(\mu r\cos\psi)$$

$$- \cos(\mu r\cos\psi)(\mu_1 r^3 \sin\psi\cos\alpha + \mu_1 r^3 \cos\psi\sin\alpha)\}\, d\psi\, r dr$$

$$= 0,$$

since $$\int_0^{2\pi} \sin(\mu r\cos\psi)\, d\psi = 0,$$

$$\int_0^{2\pi} \cos(\mu r\cos\psi)\sin\psi d\psi = 0,$$

and $$\int_0^{2\pi} \cos(\mu r\cos\psi)\cos\psi d\psi = 0.$$

Hence the intensity is proportional to the square of

$$\frac{J_1(\mu)}{\mu} + \frac{\mu_1\sin\alpha}{\mu}\left\{J_2(\mu) - \frac{2J_3(\mu)}{\mu}\right\}.$$

Again regarding the linear source as composed of luminous point sources, the illumination at Q″ in the reproduction of the Y-axis is proportional to

$$\int_0^\infty \left[\frac{J_1(\mu)}{\mu} + \frac{\mu_1\sin\alpha}{\mu}\left\{J_2(\mu) - \frac{2J_3(\mu)}{\mu}\right\}\right]^2 dY',$$

where Q″ is distant β from the element dY', and β is proportional to μ.

The method has thus been outlined for the Von Seidel aberrations. There remains the investigation due to chromatic aberration, and the effects of the higher-order aberrations on the straight-line reproductions.

Mathematics and Mechanics Dept.,
The Technical College, Cardiff.
Nov. 29, 1928.

LII. *The Nature and Form of the Contact between two Elastic Bodies pressed together by a Given Force.* *By* H. H. JEFFCOTT [*].

1. IN many engineering structures and machines various parts made of steel or other elastic material operate in contact with one another, and are pressed together by gravitational or applied forces.

It is sometimes necessary to know the values of the stresses that exist at the point of contact and the dimensions of the contact area.

The general solution of this problem, as developed by Hertz, leads to somewhat complicated results, involving, in their application to engineering problems, the solution of certain elliptic integrals. The object of this note is to carry the general solution to a further stage in which, with the aid of curves, approximate results may be readily obtained without the necessity of using tables of elliptic functions.

2. The solution of the problem of finding the nature of the contact between two isotropic elastic bodies when pressed together by a given force P has been given by Hertz. (See Love's 'Mathematical Theory of Elasticity,' 3rd edition, paragraphs 137, 138.)

Hertz supposes the surfaces in contact to be perfectly smooth, so that only a normal pressure acts between the parts in contact, and these parts are assumed to be very small compared with the whole surface. The applied force P is distributed as a pressure over the common area of contact or compressed area. It is required to find the form and dimensions of the compressed area and the pressure distribution over it.

To this end it is necessary to assign such a form to the compressed area, and to obtain such a system of displacements and stresses, that the following requirements are satisfied:—the displacements and stresses shall satisfy the differential equations of equilibrium for elastic bodies; the stresses shall vanish at a great distance from the compressed area; the tangential component of stress shall vanish all over both surfaces; the normal pressure at the surface shall vanish outside the compressed area; within the compressed area the pressure at a point on the surface of one body shall be equal and opposite to the pressure at that point on the surface of the second body; the integral of the pressure taken over the compressed area shall be equal to the total applied force of contact; the distance between the surfaces as altered by the displacements shall vanish within the compressed area and shall exceed zero outside that area.

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[*] Communicated by the Author.

It follows that the curve of compression which bounds the compressed area is approximately an ellipse. Let the principal radii of curvature of the two bodies at the point of contact be represented by R_1, R_1' and R_2, R_2', and let ω represent the angle between the normal sections of the two surfaces in which the radii of curvature are R_1 and R_2.

Let a and b represent the semi-axes of the ellipse of compression, and let E_1, σ_1, E_2, σ_2 represent Young's Modulus and Poisson's Ratio for the bodies respectively. Let α represent the total compression of the two bodies in the direction of the common normal at the point of contact. This is the distance through which the bodies approach each other under the action of the given force. Also let

$$H=\frac{1-\sigma_1^2}{E_1}+\frac{1-\sigma_2^2}{E_2},$$

$$k^3=\frac{2M}{3PH}, \quad \text{and} \quad k'=\frac{4a}{3PH}.$$

Let M and N be given by equations (1) and (2):

$$M=\frac{1}{R_1}+\frac{1}{R_1'}+\frac{1}{R_2}+\frac{1}{R_2'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$N^2=\left(\frac{1}{R_1}-\frac{1}{R_1'}\right)^2+\left(\frac{1}{R_2}-\frac{1}{R_2'}\right)^2$$
$$+2\left(\frac{1}{R_1}-\frac{1}{R_1'}\right)\left(\frac{1}{R_2}-\frac{1}{R_2'}\right)\cos 2\omega. \quad (2)$$

Then the results obtained by Hertz reduce to equations (3) to (6):

$$\pi a^3(M-N)=3PH\int_0^\infty \frac{d\theta}{\left\{\theta\,.\,(1+\theta)^3\,.\left(\frac{b^2}{a^2}+\theta\right)\right\}^{\frac{1}{2}}}, \quad (3)$$

$$\pi b^3(M+N)=3PH\int_0^\infty \frac{d\theta}{\left\{\theta\,.\,(1+\theta)^3\,.\left(\frac{a^2}{b^2}+\theta\right)\right\}^{\frac{1}{2}}}, \quad (4)$$

$$4\pi a\alpha = 3\text{PH}\int_0^\infty \frac{d\theta}{\left\{\theta.(1+\theta).\left(\frac{b^2}{a^2}+\theta\right)\right\}^{\frac{1}{2}}}, \qquad (5)$$

$$p = \frac{3\text{P}}{2\pi ab}\sqrt{1-\frac{x^2}{a^2}-\frac{y^2}{b^2}}, \quad . \quad . \quad . \quad . \quad (6)$$

if p represents the pressure at any point x, y of the compressed area.

We observe that the mean pressure $\frac{\text{P}}{\pi ab}$ is two-thirds of the maximum pressure.

When the elastic properties and dimensions of the bodies and the nature of the contact are given, we know

$$\text{H},\ \text{R}_1,\ \text{R}_1',\ \text{R}_2,\ \text{R}_2',\ \text{and}\ \omega.$$

Hence M and N are found from equations (1) and (2). Equations (3) and (4) then give a and b, and equation (5) gives the compression α.

3. The elliptic integrals contained in equations (3), (4), and (5) are somewhat troublesome to evaluate, as they require the use of Legendre's or other tables. Accordingly, curves have been drawn here, from which a, b, and α may be approximately derived in terms of M and N, and when a and b have thus been obtained, equation (6) gives the value of the pressure distribution p. These curves have been obtained in the following manner:—

The integral in equation (3), when transformed by the substitution $\theta = \cot^2\phi$, reduces to

$$\frac{2}{c^2}\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-c^2\sin^2\phi}} - \frac{2}{c^2}\int_0^{\frac{\pi}{2}} \sqrt{1-c^2\sin^2\phi}\,.\,d\phi \quad . \quad (7)$$

or $\frac{2}{c^2}(\text{F}-\text{E})$, where $c^2 = 1-\frac{b^2}{a^2}$ and F and E are the complete elliptic integrals of the first and second kinds.

The integral in equation (4) may be transformed to standard form by putting $\theta = \tan^2\phi$. It then reduces to

$$\frac{2}{c^2}(1-c^2)^{1/2}\int_0^{\frac{\pi}{2}} \sqrt{1-c^2\sin^2\phi}\,.\,d\phi$$
$$- \frac{2}{c^2}(1-c^2)^{3/2}\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-c^2\sin^2\phi}} \qquad (8)$$

or

$$\frac{2\sqrt{1-c^2}}{c^2}\{E-F(1-c^2)\}.$$

In like manner, on making the substitution $\theta=\cot^2\phi$, the integral in equation (5) reduces to

$$2\int_0^{\frac{\pi}{2}}\frac{d\phi}{\sqrt{1-c^2\sin^2\phi}}=2F. \quad . \quad . \quad . \quad . \quad (9)$$

We now have

$$\frac{2a^3(M-N)}{3PH}=\frac{4}{\pi c^2}(F-E), \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{2b^3(M+N)}{3PH}=\frac{4\sqrt{1-c^2}}{\pi c^2}\{E-F(1-c^2)\}, \quad . \quad (11)$$

$$\frac{4u\alpha}{3PH}=\frac{2}{\pi}F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Dividing equation (11) by equation (10) and reducing, we obtain

$$\frac{N}{M}=\frac{E(2-c^2)-2F(1-c^2)}{Ec^2}. \quad . \quad . \quad . \quad . \quad (13)$$

Substituting this value of $\frac{N}{M}$ in (10) and (11) and reducing, we obtain

$$\frac{2Ma^3}{3PH}=\frac{2}{\pi(1-c^2)}E \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$\frac{2Mb^3}{3PH}=\frac{2\sqrt{1-c^2}}{\pi}E. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

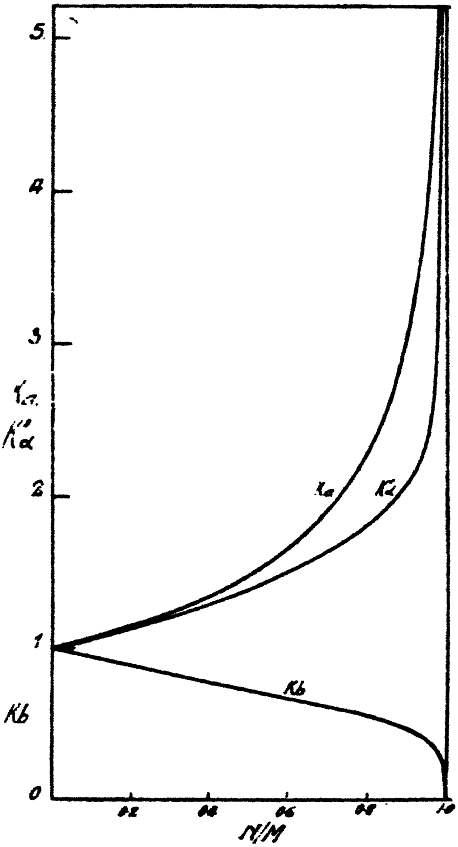
The numerical values of F and E corresponding to various assumed values of c can be obtained directly from the tables of elliptic functions.

Thus from (13) we find $\frac{N}{M}$ in terms of c, and from (14), (15), and (12) we find ka, kb, and $k'\alpha$ also in terms of c. It is convenient to plot ka, kb, and $k'\alpha$ directly in terms of $\frac{N}{M}$. This has been done in Table I. and curves (fig. 1).

TABLE I.

$\frac{N}{M}$...	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1
c...	0	·485	·647	·749	·822	·875	·917	·948	·972	·989	1
ka...	1	1·070	1·150	1·241	1·351	1·485	1·661	1·906	2·294	3·085	∞
kb...	1	·936	·877	·823	·769	·718	·664	·608	·544	·461	0
$k'a$...	1	1·068	1·140	1·216	1·300	1·392	1·503	1·636	1·816	2·100	∞

Fig. 1.



4. We may illustrate the application of these results by the following examples :—

(1) A loaded cylindrical steel wheel rests on a straight steel rail of which the upper surface is of circular cross-section. It is required to find the dimensions of the contact.

Let the radius of the wheel be represented by r_1, and let the cross-section at the upper surface of the rail be of radius r_2.

Then

$$R_1=r_1,\quad R_1'=\infty,\quad R_2=\infty,\quad R_2'=r_2,\quad \omega=0.$$

Equations (1) and (2) give

$$M=\frac{1}{r_1}+\frac{1}{r_2},$$

$$N=\frac{1}{r_1}-\frac{1}{r_2}.$$

Next, let the given dimensions and constants be

$$r_1=22 \text{ in.},\quad r_2=12 \text{ in.},\quad E_1=E_2=3\times 10^7 \text{ lb. wt. per sq. in.};$$

$$\sigma_1=\sigma_2=0{\cdot}28;\quad P=10{,}000 \text{ lb. wt.}$$

We find

$$M=0{\cdot}129,\quad N=0{\cdot}0379,\quad \frac{N}{M}=0{\cdot}294.$$

The curves give

$$ka=1{\cdot}25,\quad kb=0{\cdot}82,\quad k'\alpha=1{\cdot}205.$$

Further, we have

$$H=6{\cdot}14\times 10^{-8},\quad k=5{\cdot}2.$$

Hence $\quad a=0{\cdot}240$ in., $\quad b=0{\cdot}1575$ in.

Also $\quad k'=521\quad$ and $\quad \alpha=0{\cdot}00231$ in.

Accordingly

$$p_{\text{max.}}=126{,}000 \text{ lb. wt. per sq. in.}$$

and

$$p_{\text{mean}}=84{,}000 \text{ lb. wt. per sq. in.}$$

The ellipse of compression has semi-axes 0·24 in. and 0·157 in.

(2) A spherical steel ball is pressed between the jaws of a measuring machine by a known force. It is required to find the consequent diminution of its diameter.

Let the radius of the ball be denoted by r.

Then $\quad M=\dfrac{2}{r}\quad$ and $\quad N=0,$

since $\quad R_1=R_1'=r\quad$ and $\quad R_2=R_2'=\infty.$

Hence $\dfrac{N}{M}=0$, and from the curves $ka=kb=1$, $k'\alpha=1$.

Suppose we are given that the diameter of the ball is $\frac{1}{4}$ inch, that the force applied by the flat jaws is 10 lb. wt., and that $E_1 = E_2 = 3 \times 10^7$ lb. wt. per sq. in. and $\sigma_1 = \sigma_2 = 0 \cdot 28$.

Thus $r = \frac{1}{8}$ in., and $H = 6 \cdot 14 \times 10^{-8}$.

Hence $k = 259$, $\therefore$ $a = b = 0 \cdot 00386$ in.

Finally $k' = 8391$, $\therefore$ $\alpha = 0 \cdot 000119$ in.,

so that the total compression of the diameter due to the contacts is approximately 0·00024 in.

LIII. *A Criticism of the Electron Theory of Metals.*

By H. Monteagle Barlow, *A.M.I.E.E., Ph.D.*[*]

Introduction.

IN Sommerfeld's recent attempt to reinstate the electron theory of metallic conduction, the physical hypotheses of the classical treatment are employed without alteration [†]. The only innovation is the supposition that the "electron gas" interpenetrating the atoms of the metal is "degenerate," and therefore does not obey the classical gas laws. The theory assumes a particular form of "degeneration" based on quantum considerations.

After analysing a large number of spectroscopic observations, Pauli concluded that no two electrons in an atom could occupy equivalent orbits, characterized by the same energy values [‡]. Fermi, Dirac and others have extended this principle of exclusion to the particles in a gaseous assembly, and shown that for an ideal gas the degree of "degeneration" depends upon the number of particles possessing the same set of quantum numbers [§].

Thus, in a "non-degenerate" assembly all the possible stationary states are quite distinct. This extension of Pauli's principle has no apparent physical basis except in so far as a large number of molecules forming a gaseous assembly can be compared with the electrons in a single atom. Ordinary gases are supposed to have a very large number of available energy values for their particles at normal temperature and pressure. Hence two or more such particles never want to get into one cell and possess the same "characteristics." The assembly is said to be "non-degenerate" except under high compression and low temperature. On the other hand, Sommerfeld has shown that in a metal the hypothetical electron gas, to which is attributed conduction of heat and electricity, is normally highly "degenerate" in the sense of the Fermi statistics, principally on account of the very small mass of its particles [*].

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[*] Communicated by the Author.

[†] Sommerfeld, *Naturwissenschaften*, Oct. 14, p. 63 (1927); and *Zeits. für Phys.* xlvii. pp. 1 & 43 (1928).

[‡] W. Pauli, Jr., *Zeits. für Phys.* xxxi. p. 765 (1925).

[§] Fermi, *Zeits. für Phys.* xxxvi. p. 902 (1926); Dirac, Proc. Roy. Soc. A, cxii. p. 661 (1926); Fowler, Proc. Roy. Soc. A, cxiii. p. 432 (1927).

In working out this idea, Sommerfeld arrived at a number of interesting conclusions, and others have amplified and extended his work [†]. Recently two valuable papers by Prof. E. H. Hall have been published giving a carefully-considered criticism of the theory and the results to which it leads [‡]. His view is that the new hypothesis regarding the laws governing the electron gas has not been justified, and that the simple classical theory actually gives a better interpretation of some of the facts. One of the consequences of applying the Fermi statistics to the electron gas is to give it a pressure at the zero point amounting to some 100,000 atmospheres, and at normal temperature a still higher value. In the absence of any definite information, the concentration of the free electrons is assumed to be about one per atom under ordinary conditions. This concentration is supposed to vary with temperature and mechanical pressure, but no attempt is made to define these changes, which, Sommerfeld remarks, "can only be explained by a deeper treatment."

Many of the earlier modifications of the classical theory also employ a free electron density which is taken as a function of temperature [§], and Prof. Hall, after commenting on the introduction of this idea into the Sommerfeld theory, says: "Since my own theory of metallic conduction etc.

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[*] See also Pauli, *Zeits. für Phys.* xli. p. 81 (1927).

[†] Eckart, *Zeits. für Phys.* xlvii. p. 38 (1928); Fowler, Proc. Roy. Soc. A, cxvii. p. 549 (1928); Houston, *Zeits. für Phys.* xlvii. p. 33 (1928); Borelius, *Ann. der Phys.* lxxxiv. p. 907 (1927); Frenkel, *Zeits. für Phys.* xlvii. p. 819 (1928); Nordheim, *Zeits. für Phys.* xlvi. p. 833 (1928); Houston. *Zeits. für Phys.* xlviii. p. 449 (1928); Kretschmann, *Zeits. für Phys.* xlviii. p. 739 (1928); Nordheim, Proc. Roy. Soc. A, cxix. p. 689 (1928); Frenkel & Mirolubow, *Zeits. für Phys.* xlix. p. 885 (1928); Lennard-Jones & Woods, Proc. Roy. Soc. A, cxx. p. 727 (1928); Waterman, Phil. Mag. vi. p. 965 (1928).

[‡] Hall, Proc. Nat. Acad. Sci. xiv. pp. 366 & 370 (1928).

[§] Hall, Phys. Rev. xxviii. p. 392 (1926) and Proc. Nat. Acad. Sci. (1927); Caswell, Phys. Rev. xiii. p. 386 (1919); Waterman, Phys. Rev xxii. p. 259 (1923).

has, I believe, sometimes been criticized as involving a considerable number of assumptions of a more or less special character, I am interested in these evidences that the new theory cannot get on without similar inventions. Variation of n (number of free electrons per cub. cm.) with temperature has been one of my cardinal hypotheses." Later he gives a brief review of his dual theory, in which he puts [*]

$$n=z\mathrm{T}^{q},$$

where z and q are constants and T the absolute temperature. Such variations in the density of the conduction electrons are a logical development from the classical theory, and the position is not materially altered by the introduction of the new statistics.

It is important, therefore, to consider how far experiment confirms this assumption regarding the free electron concentration, and whether we are really justified in treating the ionized negative charges as though they form a gaseous atmosphere interpenetrating the atoms of the metal.

Reasons for Doubting the Validity of the Gas Hypothesis.

Some time ago Lindemann advanced a strong argument, pointing out that the normal forces between the free electrons might be expected to make the assembly behave like a perfect solid rather than a gas [†] Even before the electron theory was invented, Maxwell and his contemporaries had come to the conclusion that one of the most fundamental properties of the electric fluid responsible for a current in a conductor was its incompressibility [‡].

The statement that the divergence of the electric force is zero in the interior of a metal, not only expresses the fact that no electricity can be created or destroyed, but also that there can be no accumulation of electricity. This seems to be a natural deduction from the following experimental observations: firstly, that the charge absorbed by a condenser does not depend in any way upon the nature or thickness of the metal plates; and, secondly, that there is no definite indication of any change in the resistance of a conductor when surrounded by an intense electric field.

It is practically certain that the positive nuclei of the atoms of a metal are fixed in position so that, if a charge distributed throughout the volume is impossible, it must be equally impossible to alter the concentration of the negative particles, including among others the free electrons.

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[*] Hall, Proc. Nat. Acad. Sci. xiv. pp. 377 & 802 (1928).

[†] Lindemann, Phil. Mag. xxix. p. 127 (1915). See also Wolf, Phys. Rev. xxvi. p. 256 (1925) and Hume-Rothery, Phil. Mag. iv. p. 1017 (1927).

[‡] Maxwell, 'Scientific Papers.'

The supposition that the number of free electrons per cub. cm. increases with the temperature is not really consistent with the hypothesis that they form a gaseous atmosphere. For example, it is difficult to explain on that basis how thermal conduction can proceed without building up a considerable charge along the conductor in the direction of the temperature gradient. If the conduction of heat is to be regarded as the result of convection currents in what is equivalent to a gas occluded within a porous body, the simple hypothesis that the free electrons at the hot end of a metal bar are more numerous and have greater kinetic energy than those at the cold end is quite inadequate. Hall found it necessary to assume that the "associated" electrons, which pass from one atomic union to another without sharing the heat energy, also take an important part in the conduction process.

The gas theory is less illuminating when applied to explain the Thomson effect. Without any evidence to show that unneutralized electricity can exist in the interior of a conductor, it is hardly justifiable to suppose that unequal heating sets up an electric field by variations in the number of free electrons crossing different sections.

Another case in which the gas hypothesis is unsatisfactory is that of an insulated metal bar moving at right angles to its length and perpendicular to a magnetic field. The E.M.F. induced in it produces an accumulation of negative electricity towards one end and a corresponding deficiency towards the other. The force which tends to displace the mobile electricity in the bar acts on the individual electrons, and must operate with equal intensity over the whole cross-section.

If the electric fluid resembles a gas, one would naturally expect the free electrons in the interior of the metal, as well as those at the surface, to drift along the length and build up a charge throughout the volume. The E.M.F. increases with the length of the bar, and the pressure on the free electrons must rise gradually from one end to the other, so that it seems impossible to maintain equilibrium between the forces when unneutralized electricity can only exist on the surface.

A similar inconsistency becomes apparent when considering the electrical effect of rotating a disk at a high speed about its axis. Since an electron has a finite mass, the radial acceleration would be expected to produce an accumulation of negative electricity towards the circumference, and it is clearly quite impossible to balance the centrifugal force on the supposed gaseous atmosphere of free electrons in the interior, if their concentration remains unchanged. In spite of the fact that all these difficulties must be well known, it appears from recent developments that the idea of an electron gas between the atoms of a metal is by no means discredited. Obviously, an incompressible fluid cannot have the properties of a gas, and the all-important question to decide, therefore, is whether the conducting fluid is strictly incompressible or not. The author has attempted to give a conclusive answer to this question by an appeal to direct experiment.

EXPERIMENTAL WORK.

Three different methods of investigation were employed.

1. *Experiments on the Electrical Effect of Accelerating a Conductor.*

Prof. Tolman and his co-workers have shown that when a conductor, moving with a high velocity in the direction of its length, is suddenly brought to rest, a current is produced during the retardation such as would result from mobile electricity in it having a negative charge *. The conductor formed part of a closed circuit, so that in this case the effect would have been the same whether the conducting fluid were incompressible or not.

In the following experiments (figs. 1 & 2) two copper disks rotating side by side in opposite directions at 3000 R.P.M. were employed to build up a negative charge at the circumference of the combination, which was independent of the effect of the earth's field. Spoonfuls of electricity were carried across from the rim of the two disks to an insulated annular trough of small capacity connected to the needle of a Lindemann electrometer.

In some of the experiments mercury was fed in at the centre to the small space separating the disks, and the centrifugal force flung it out between the amalgamated surfaces, which it left in the form of globules after assuming their joint potential. Electrification of the mercury by "splashing" was made small by running the apparatus in air at reduced pressure (4 mm.) or in pure hydrogen.

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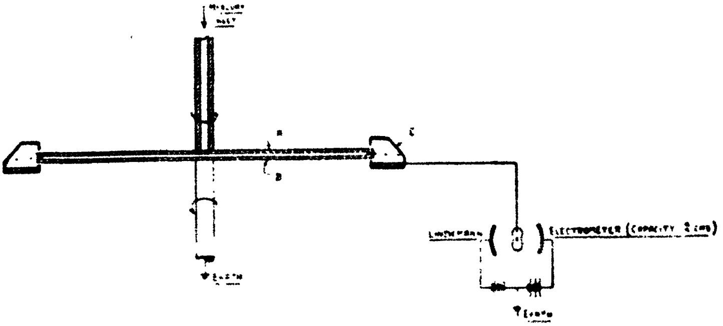
* Tolman & Stewart, Phys. Rev. iii. p. 97 (1916) and Phys. Rev. ix. p. 164 (1917); Tolman, Karrer, & Guernsey, Phys. Rev. xxi. p. 525 (1923); Tolman & Mott-Smith, Phys. Rev. xxviii. p. 794 (1926).

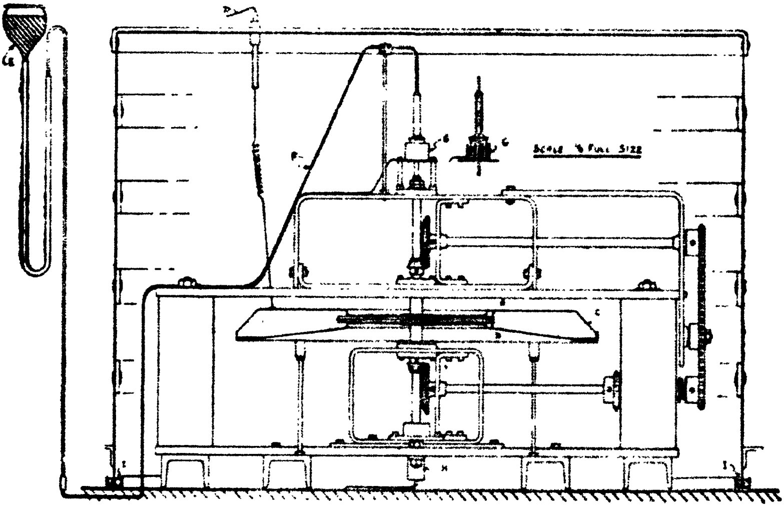
Another method of transferring the electricity from the disks to the surrounding trough without employing mercury was as follows:—A number of small copper blocks, all exactly the same size, were attached to the circumference of the disks by soldering them to fine wires projecting from it. Each disk had the same number of these blocks or bullets, and at a certain speed the centrifugal force was sufficient to break the wires, so that the bullets left the disks to be deposited in the surrounding trough.

Fig. 1.



SKETCH SHOWING PRINCIPLE OF MERCURY APPARATUS

Fig. 2.



The result of these experiments was to show that as much as two cub. cms. of metal flung off the rotating disks did not carry with it more than 10^{-11} *coulomb of electricity.* According to the simple gas theory this figure is at least 100,000 times too small, showing that any excess electricity on the bullets must have been practically confined to the surface. The very feeble charge that did appear on the trough was negative.

In dealing with the acceleration effects, an experiment was also made on the same principle as that employed by Tolman (figs. 3 & 4). A phosphor-bronze rod, 2 feet 6 inches long, was allowed to fall freely under gravity in the direction of its length through a height of 66 ft., and then brought suddenly to rest at the bottom. The rod formed part of a closed electric circuit, which included a transformer whose secondary winding was connected with a three-valve amplifier with a Paschen high sensitivity galvanometer in the output. The guide-wires for the rod were used to make electrical connexion with it by means of ball contacts amalgamated with mercury.

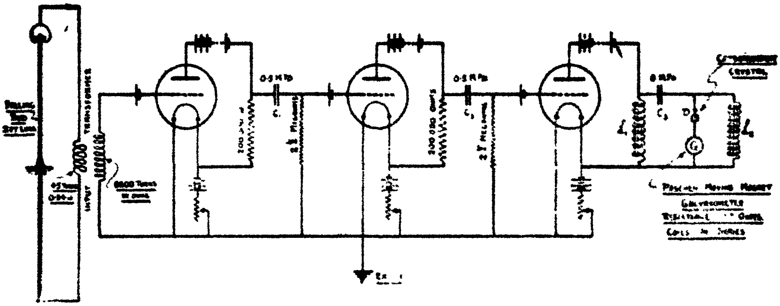
The current impulses obtained with this apparatus were in the direction anticipated, and their average value was of the right order of magnitude, although the individual figures varied considerably. Spurious effects made the result qualitative rather than quantitative, but the author is not aware of any other experiments that have been made to verify the work of Tolman and his assistants.

2. *Experiments on the Total Displacement of Electricity in an Insulated Conductor subjected to an Induced E.M.F.*

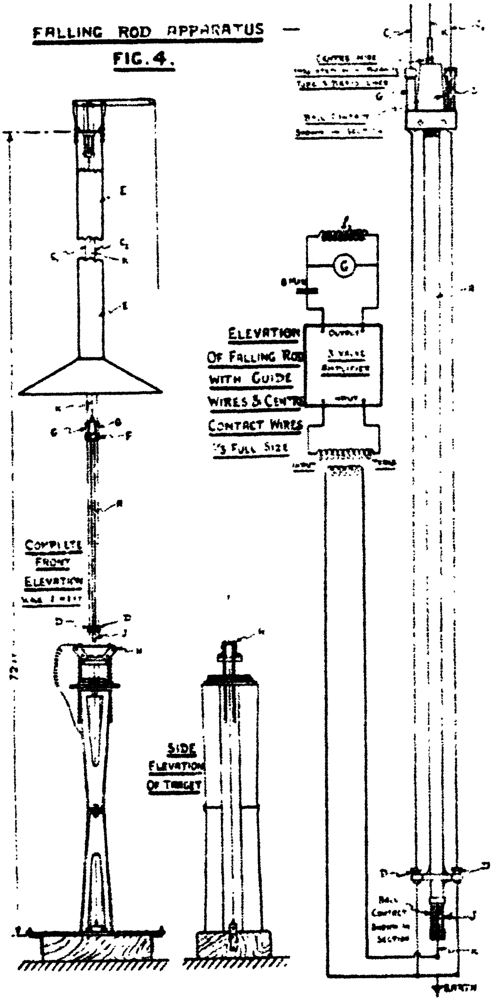
The mechanical force on the free electrons due to the radial acceleration in the rotating disks previously described was necessarily small under any conditions.

By employing one disk only with a magnetic field to generate an E.M.F. of about a volt between the centre and circumference, the force tending to squeeze the electrons up towards the rim was considerably increased (fig. 5). If the charge on the disk were not entirely confined to the surface, it seemed necessary to suppose that the unneutralized electricity in the interior must be shielded in some way, so that it added nothing to the induction on the surrounding cylinder. Arrangements were made, therefore, to break the earth connexion at the centre of the disk when rotating, and then to bring the apparatus to rest, the deflexion of the electrometer being carefully observed during the whole process to see if any changes occurred.

DIAGRAM SHOWING AMPLIFIER & GALVANOMETER CONNECTIONS FIG.

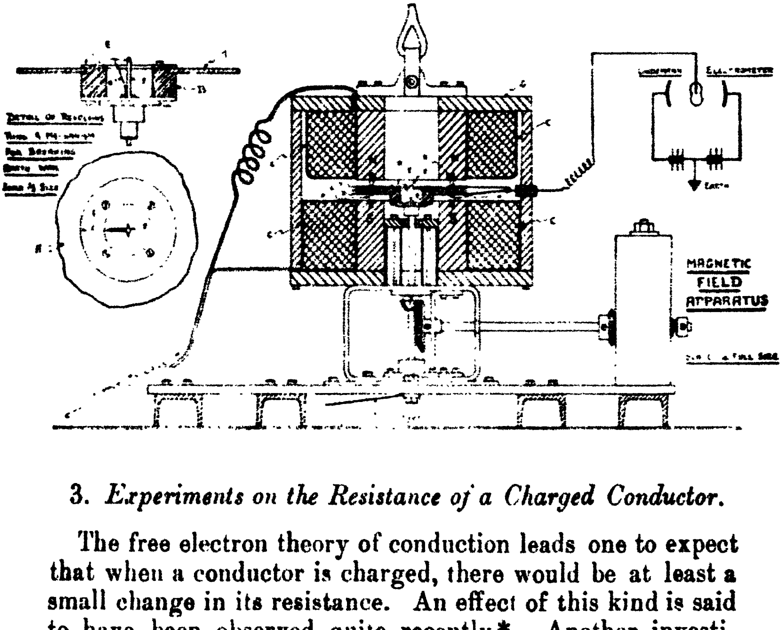


FALLING ROD APPARATUS —
FIG. 4.


E
C_2
C
K
E
G
F
R
COMPLETE FRONT ELEVATION
D
J
H
72 in
SIDE ELEVATION OF TARGET
H
C
K
CENTRE WIRE
G
BALL CONTACT SHOWN IN SECTION
ELEVATION OF FALLING ROD WITH GUIDE WIRES & CENTRE CONTACT WIRES 1/3 FULL SIZE
L_2
G
8 MFD
OUTPUT
3 VALVE AMPLIFIER
INPUT
R
D
D
BALL CONTACT SHOWN IN SECTION
J
K
EARTH

Assuming that the electricity squeezed into or out of the disk resided on the surface only, it was found that the potentials calculated from the capacity of the system agreed within 1 *per cent. with the actual observations, and these potentials were not reinforced at any time by unneutralized electricity making its appearance from the interior of the conductor.* Copper, brass, lead, and graphite disks of the same dimensions all stored the same quantity of electricity, and when the inside of the brass disk was removed, leaving a thin shell so that the capacity remained unchanged while the mass was halved, there was no alteration in the electrometer readings.

Fig. 5.



3. *Experiments on the Resistance of a Charged Conductor.*

The free electron theory of conduction leads one to expect that when a conductor is charged, there would be at least a small change in its resistance. An effect of this kind is said to have been observed quite recently[*]. Another investigator made a similar claim in 1921, but it was afterwards shown to be spurious[†]. Some earlier experiments by Bose also gave a negative result[‡].

In the following investigation the measurements were made with a simple Wheatstone bridge, the conductor under observation being charged by electrostatic induction employing either steady electric fields or alternating electric fields of 100,000 frequency (fig. 6). Some very thin films of platinum were prepared by depositing colloidal paint on the outside of a thick glass capillary tube to form a U-shaped conductor (fig. 7). Under a microscope the films appeared quite continuous, although their thickness, in some cases, did not exceed 2 micro-millimetres. Two charging electrodes

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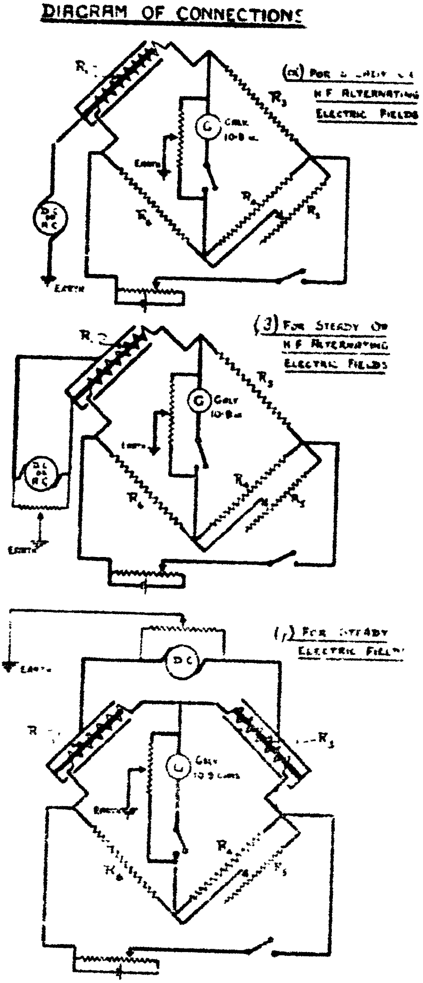
[*] Pierucci, *Accad. Lincei Atti.* vii. p. 400 (1928).

[†] Perkins, Phys. Rev. xviii. p. 131 (1921). Contradicted by Wenner, Forman, & Lindberg, Phys. Rev. xx. p. 589 (1922).

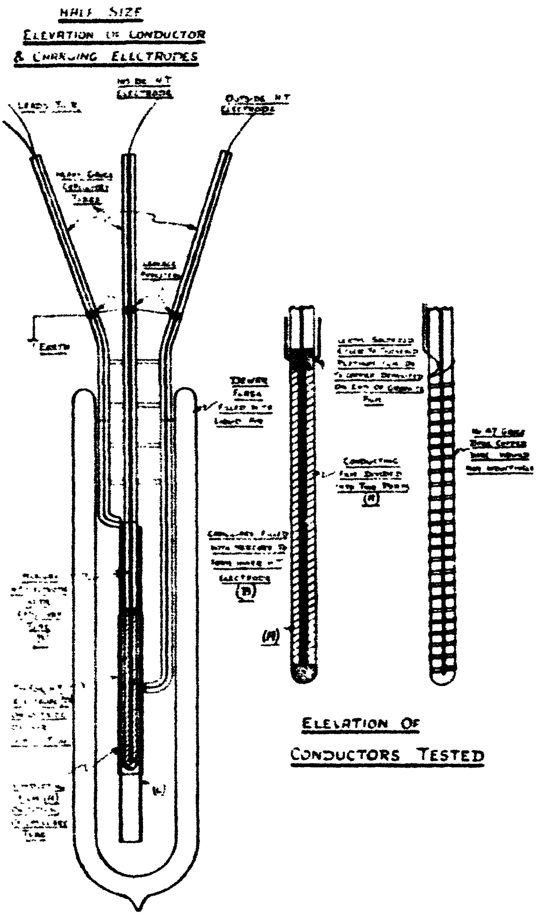
[‡] Described in Sir J. J. Thomson's 'Corpuscular Theory of Matter,' p. 83 (1907).

Fig. 6.



were provided so that both sides of the film could be electrified simultaneously, and the whole equipment was immersed in liquid air. Some experiments were also made with graphite films and 47-gauge bare copper wire.

Fig. 7.



In no case did the charging or discharging of the conductor produce an instantaneous and reversible change in the resistance. There was a slight heating effect, but this was easily distinguishable because it took a minute or two to become appreciable. The accuracy of the observations was limited by the tendency by the films to become unstable. In very intense electric fields irregular resistance changes of a more or less permanent nature appeared, presumably brought about by a re-arrangement of the molecules of the metal.

The most sensitive measurements were made with two platinum films, one in each of the adjacent arms of the bridge (fig. 6 (γ)).

In this case the estimated thickness of the films was about nine molecules each, and the charge on every square cm. of the surface was equivalent to an excess or deficiency of 4×10^{11} *electrons on the inside and* $1{\cdot}7\times10^{11}$ *electrons on the outside; yet there was no change in the resistance greater than* 0·0012 *per cent.* The type of change referred to here is one which appears as soon as the charge is produced, and disappears immediately the charge is removed.

Conclusions.

The foregoing experiments prove conclusively that the assembly of free electrons in the interior of a conductor invariably behaves like a perfectly incompressible fluid, and consequently in no way resembles a gas. The fundamental hypothesis of the Sommerfeld theory of conduction cannot, therefore, be maintained.

Finally, the author desires particularly to express his thanks to Prof. J. A. Fleming, M.A., D.Eng., D.Sc., F.R.S., for giving so freely of his time and experience in the development of these investigations, and also gratefully to acknowledge the facilities granted by Prof. Fleming and Prof. Clinton for carrying out the experimental work.

University of London,
University College,
Gower Street, W.C. 1.
December 1928.

LIV. *The Phenomena of Projected Electrons.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IT has been suggested to me that I should state more definitely the conclusions which can be deduced from a recent note[*] of mine with regard to the Einstein theory of Relativity.

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[*] "A Note on the Problem of the 'Mass' of a Moving Electron" (Phil. Mag. vol. v. p. 636, March 1928).

In the first place, the argument refers to the form of the electric lines of force near to a plane conductor, when an electron is moving away from that boundary; while the application refers to the motion of the electron, as it emerges from the slit of a condenser formed of two conducting plates (as in the Bucherer type of experiment). But, although the use of the plane boundary would give a poor estimate of the actual effects of the conductors, yet it illustrates the kind of disturbance of the field which must take place; so that near to the condenser, *the lines of force must deviate from perfect symmetry*, and it is therefore evident that the electrons are *retarded* during their flight from the opening or slit of the condenser into that part of the space where the velocity can be regarded as finally steady. It would be almost impossible to calculate the deviation that takes place, during this retardation, with any degree of accuracy; but, by means of fairly simple considerations, I have convinced myself that the deviation near the slit is small compared with the probable errors of observation. Thus, the deviations observed by Bucherer (and by later experimenters) can be calculated with quite sufficient accuracy by means of the Lorentz-formula; and this agrees with the numerical results found by Lorentz himself, and in similar calculations made with reference to other experiments (of the same general type as those of Bucherer).

Secondly, working on the basis of the Lorentz-formula, in recent experiments it appears that the average speed v of the electrons must be such that $\beta\,(=v/c)$ is at least ·9; in some cases a value as high as ·95 has been recorded. Now, in view of the retardation already mentioned, it is clear that the velocity with which the charged particle leaves the slit must be *greater* than that with which the steady path is described finally. Taking these two points into consideration it is not unreasonable to suppose that *at the slit itself*, $v=c$. In verbal discussions of these ideas, the usual objection to the possibility of motion at speed $v=c$ is raised, that this suggestion involves *infinite energy*, in view of Lorentz's formula [*]

$$\frac{2}{3}\frac{e^2}{a}\frac{1}{\sqrt{1-\beta^2}}$$

where, as above, we write $\beta=v/c$.

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[*] The factor 2/3 corresponds to a surface-density; it is changed to 4/5 for a volume-density. See, for instance, G. A. Schott, 'Electromagnetic Radiation,' Arts. 143 and 240.

To discuss this argument, it is desirable to recall the method used by Lorentz in obtaining his formula; the electron is reduced to rest by applying the Lorentz-transformation; and the transformed field is assumed to be of the simple radial type, associated in electrostatics with a uniform surface-density on a spherical conductor. That is, *the transformed field is supposed to extend to infinity*; this assumption will not be likely to affect the character of the field near to the electron itself, but it has considerable influence on the result found for the energy. In all known wave-solutions [*], there is a pulse or skin (to use Heaviside's own term), which travels with speed c; this pulse separates two distinct fields from each other, and the energy in the pulse is of the same order as that in the interior [†].

Thus Lorentz's formula implies that no account is taken of the outer boundary of the field; and so far, any attempt to extend his method to take such account has failed. But we may use the solution roughly indicated in my former note; and this gives some idea of the magnitudes involved. Supposing that the electron can be maintained at a velocity equal to c, the pulse will always contain the electron, the field beyond the pulse being either simply electrostatic, or else zero; and the lines of electric force will be condensed into the thin skin (its thickness will be equal to the diameter of the electron). The formula for the energy which corresponds to Lorentz's quoted above is then

$$\frac{e^2}{a}\left\{\log\left(\frac{R}{a}\right)+1\right\},$$

where R is the radius of the central sphere of the pulse.

Under the conditions of the Bucherer experiment R cannot exceed the radius of the cylinder on which the photographic plates are bent, so that R may be supposed of the order of 10 to 20 cm.; and for β-particles the radius a will be of the order 10^{-13} cm., which makes the bracket in the last formula about equal to 34. This is roughly twice the numerical factor derived from the Lorentz formula, if we suppose $\beta = \cdot 999$. It would seem clear therefore that the statement that $v=c$ involves infinite energy is misleading.

Thirdly, having accepted as a working hypothesis that the electrons leave the slit at a speed $v = c$, we naturally inquire whether such a speed can be maintained *between the plates of*

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[*] See, for instance, G. A. Schott, *l. c.* ch. v. (see pp. 75, 76, for typical diagrams); and Heaviside, 'Electromagnetic Theory,' vol. i. pp. 55–62, and vol. iii.

[†] Heavside, 'Electromagnetic Theory,' vol. iii. pp. 127–134.

the condenser itself. Now, the extremely simple solution briefly stated in my note[*] shows that, at speed $v = c$, the lines of force remain in planes perpendicular to the line of flight, and thus *no retardation occurs in the direction of the line of flight.* As regards the transverse electric force, this is neutralized (as in the usual version of the theory) by the crossed magnetic field. It follows that *between the plates of the condenser, a steady motion, parallel to the plates, is possible at the special speed $v = c$.* The objection may be urged that it is unlikely that every charged particle will be ejected from a radioactive substance at the precise speed $v = c$. Now, if at the instant of ejection $v < c$ (since there is no source of subsequent acceleration), the speed will never attain the value $v = c$; accordingly, we must suppose that, initially, $v \geqq c$. As regards the case $v > c$, the only detailed solutions at present known are due to Heaviside[†]; these refer to charged particles moving in an unlimited space, and they indicate that the lines of force, as they leave the electron, must be bent back so as to lie within a cone of vertical angle 2α, where $\sin \alpha = c/v$. At a later stage the lines of force must turn so as to cut the plates of the condenser orthogonally, but the resultant force on the charged particle is due to the direction in which the lines of force *leave* the particle; thus there must be a marked retardation at speeds greater than c. It does not appear to be possible to make any exact determination of the distance through which a particle would travel at these high speeds; but, if the formula for the retardation, originally found by Sommerfeld[‡], is used, the distance cannot exceed a moderate multiple of the radius a; for example, if the speed is $v = \frac{3}{2}c$, the Sommerfeld formula for retardation, when multiplied by $12a$, gives an energy nearly equal to that found in our previous calculation (of the energy of an electron emerging from the slit). Consequently, if a charged particle should be ejected from the radioactive substance at a speed $v > c$, the particle will be retarded at once, and the speed will accordingly be reduced until the value $v = c$ is reached, *after which the speed can be maintained at this constant value, between the plates of the condenser, without assuming that any external force is applied.*

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[*] To all intents and purposes this result is due to Heaviside; although I have not noticed that he ever actually gave the particular interpretation which is stated in my note.

[†] See, for instance, his 'Electromagnetic Theory,' vol. iii. § 465 and §§ 497–498; some examples with $v = c$ are given in §§ 499–500. I have succeeded in obtaining some extensions of these solutions which throw further light on the character of the fields in the *pulse*; but for our immediate purposes the results given by Heaviside will be sufficient.

[‡] Calculated by Sommerfeld ('Göttingen Nachrichten,' 1905) for a particle moving in unlimited space as equal to $\frac{9}{4}\frac{e^2}{a^2}\cot^2\alpha$; this is obtained by more elaborate methods, but these would not (as far as I can see) be successful in taking any account of the plates of the condenser.

It may not be out of place to refer to the fact that the existence of such cones has been detected experimentally in photographing the flight of a bullet at speeds greater than that of sound. See, for instance, P. P. Quayle, Franklin Institute, vol. cxciii. p. 627 (1922).

The question may now be raised, as to the energy required here, if the electron moves with speed c between the plates of the condenser. An exact solution is then possible for the case when the electron is supposed to remain spherical, and to move parallel to a plane conductor; and for the present problem an approximation is possible, in consequence of the minuteness of a compared with the other dimensions; neglecting terms of the order $(a/h)^2$, it appears that the formula above will represent the energy, provided that R is replaced by

$$R = \frac{h}{\pi} \sin\left(\frac{\pi b}{h}\right),$$

where h is the distance between the plates of the condenser, and b is the distance of the centre of the electron from the nearer plate. Thus, if h is large compared with b, we can use $R = b$, which agrees (to the same order) with the value deduced from the more complete solution available when there is only one plane boundary. It follows that the energy required is of the same order as in the estimate made earlier (for an electron emerging from the slit of the condenser).

Accordingly, I put forward the suggestion that the high-speed particles may start originally with $v > c$; they will then be retarded until the speed $v = c$ is attained; afterwards they will move steadily (*without external force*) parallel to the plates of the condenser; when the slit of the condenser is passed, the particles will be again retarded, in a manner which depends on how the lines of force bend backwards (so as to cut the faces of the condenser orthogonally). The part of the later flight which produces the observed deviations will be described practically under the conditions of the Lorentz-formula (a steady value of $v < c$).

The question will now suggest itself:—How do these conclusions affect the theory of Relativity? Regarded as a branch of modern Pure Mathematics, it is evident that the theory is entirely unaffected by any questions of Physics; just as the existence of Weierstrass's and other nondifferentiable functions is not affected by the fact that no one has yet made a graph to which a tangent cannot be drawn. And, so far as the supporters of Relativity are content to regard their theory as having enlarged the region of applications of the Absolute Calculus of Levi-Civitá (and of other Italian geometers), there is nothing to prevent them from pushing their analysis to the uttermost limits of refinement.

But, when we consider the question as to how far the theory of Relativity has any direct bearing on Physics, it seems to me that, so far, we can only regard the theory as having grown out of Lorentz's simplified method of calculating the deviations observed by Bucherer. Thus I suggest that its importance consists mainly in having provided the most convenient way of carrying out the necessary analysis. To take an illustration from a cognate subject, it would appear to be on much the same footing as the Euclidean theory of parallels, which may be regarded as the simplest theory consistent with observations. It is known that other investigators have established more complicated non-Euclidean geometries ; but, within the limits of the best astronomical work, nothing has yet been observed to distinguish between the three kinds of geometry (hyperbolic, elliptic, and ordinary Euclidean). Thus, for working purposes we are justified in using only Euclidean geometry (as the simplest of the three) ; but certainly this does not enable us to assert that no distinction will ever be discovered with further refinements of instruments. In the same way, the mere fact that the Lorentz-formula gives the most elegant method of dealing with Bucherer's experiments is a very slight basis for the assumption that charged particles cannot travel at a speed $v=c$ or $v>c$.

Naturally, the objection will now be urged that the theory of Relativity has been applied with success to other problems. Let us consider first the astronomical problem of the motion of the perihelion of Mercury. In actual fact the value of $\beta=v/c$ is of the order 10^{-4} in this case ; and thus, since

$$1/\sqrt{(1-\beta^2)}=1+\tfrac{1}{2}\beta^2+\tfrac{3}{8}\beta^4+\tfrac{5}{16}\beta^6+\ldots,$$

it is evident that, even with the best astronomical instruments, no distinction can be made here between the Lorentz-formulæ and the formulæ given earlier by Larmor *, who expanded the electromagnetic equations in powers of β, retaining terms of the order β^2. Thus here, again, the

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* In his Adams Prize Essay, "Æther and Matter," ch. xi.

preference for the Lorentz-formula rests on an appeal to Pure Mathematics; for it has been found [*] that the resulting analysis is made simpler and more elegant by using Lorentz's methods. The same argument applies (with even more force) to the conclusions drawn from the Michelson-Morley experiment: for in that the value of β is less than for Mercury, so that the distinction between $1/\sqrt{(1-\beta^2)}$ and $1+\frac{1}{2}\beta^2$ cannot be observed with our present instruments.

The last "*proof*" of the theory of Relativity, and one which is often assumed to be conclusive, is based on observations of the bending of light-rays, produced by the sun's gravitation; the results are well known from the reports of recent eclipse-expeditions. Such observations certainly justify the inference that the phenomena of light and of gravitation have an intimate connexion; but the exact formulæ, originally put forward as representing the consequences of Einstein's theory, have been repeatedly criticized by Sir Joseph Larmor. An adequate summary of his arguments would occupy too much space here; but we may refer to his address to the Royal Society of Edinburgh [†] (on the presentation of the James Scott Prize) for a synopsis of his reversion to common space and time (from the relativist point of view).

Writing from a mathematical standpoint I should like to acknowledge the debt which all students of the mathematical theory of pulses and of electromagnetic waves owe to the brilliantly successful experiments of the past 30 years; without such experimental knowledge the best attempts at mathematical solutions would be valueless, owing to lack of any knowledge as to the orders of magnitude involved [‡].

I have the honour to be, Gentlemen,

Your obedient servant,

Cambridge.
12 May, 1928.

T. J. I'A. BROMWICH.

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[*] See, for instance, the account of the Dynamics of a moving electron in G. A. Schott's Adams Prize Essay ("Electromagnetic Radiation," Cambridge, 1912, pp. 257–325).

[†] Larmor, Proc. Roy. Soc. Edinb. vol. xlvii. p. 307 (1927); see, in particular, pp. 320–325, for considerations dealing with the gravitational problem.

[‡] I take the opportunity of expressing my personal indebtedness to various friends who have put at my service their knowledge of the physical circumstances of the Bucherer experiments and of the results derived from these and other works connected with them.

For some instructive remarks on the information to be derived from experiments and from mathematics, the reader may consult Heaviside's 'Electromagnetic Theory,' vol. iii. pp. 472–478, and pp. 131–134 the latter containing the first attempt to connect numerically the "*mass*" and charge of these particles.

LV. *A New Transformation in Alternating Current Theory, with an Application to the Theory of Audition.* By BALTH. VAN DER POL, *D.Sc.*[*]

[Plate VII.]

IN ordinary linear alternating current theory an inductive reactance is usually represented by $+j\omega L$, while a capacitive reactance is denoted by $-\frac{j}{\omega C}$. Therefore the *imaginary* part of an impedance may have a positive as well as a negative sign. As long as positive resistances only were known, the *real* part of an impedance was always positive (independent of the constitution of the network considered). But with the advent of negative resistances (such, *e. g.*, as the arc, the dynatron, or the triode with retroaction), the real part of an impedance, like the imaginary part, may have both signs.

The transformations to be considered here (and which may be called *j-transformations*) consist of multiplying all complex impedances of a network by j, j^2, j^3, and j^4 respectively, where $j=\sqrt{-1}$. Though *mathematically* these transformations obviously only represent a turning of the impedance vectors by angles $\pi/2$, π, $3/2\pi$, and 2π respectively, the *physical* interpretation of these transformations may lead to some new circuits or to, at first sight, unexpected relations between circuits with well-known properties.

Obviously the j^4-transformation transforms the circuit into itself, and therefore does not yield anything new. On the other hand, the j^2-transformation implies the multiplication of any circuit element with -1. This means that in the network considered every positive resistance is to be replaced by a negative resistance of the same absolute amount and *vice versâ*, and also every positive capacity by a negative capacity and *vice versâ*. With this physical interpretation of the j^2-transformation any network thus transformed retains its impedances (but multiplied by -1) *for all frequencies*. The necessity of constructing *negative inductances* and *negative capacities* does not (at least on paper) yield any difficulties now that negative resistances are at hand; for the equivalent network of fig. 1 *a* is fig. 1 *b*, as can be easily verified.

We can therefore, with the aid of two positive and one negative resistance and a capacity, construct a negative inductance which is independent of frequency. The circuit of fig. 1 *a* thus behaves exactly as if between the terminals A–B a negative inductance were inserted of amount $L=CR^2$.

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[*] Communicated by the Author. Paper read at the U.R.S I. Meeting, Brussels, Sept. 1928.

Similarly, a negative capacity (again independent of frequency) may be obtained as in fig. 2, which speaks for itself *. Thus the network of fig. 2 *a* is equivalent to a negative capacity of amount $C=LR^{-2}$ (fig. 2 *b*), as is easily verified. Of course, instabilities often arise in circuit comprising, *inter alia*, negative resistances. The stability of such a circuit can, however, be calculated. We therefore imagine with Barkhausen (*Phys. Zschr.* xxvii. p. 43, 1926) a small inductance to be inserted in series with an arc, and a small capacity to be shunted to a dynatron or triode. This system can then further be investigated with the aid of the Hurwitz determinants, giving the conditions that the real part of all the roots of an equation are negative. (I found that these determinants can be considerably simplified, and hope to report on this subject shortly.)

Fig. 1 *a*.

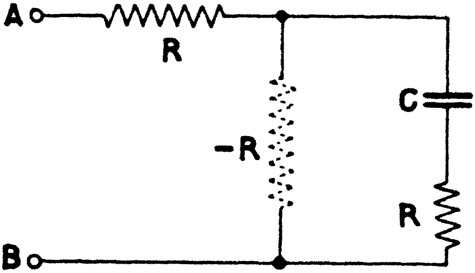
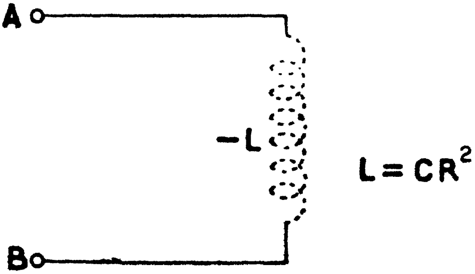


Fig. 1 *b*.



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* See Bartlett, Journal of Inst. of Elect. Eng. (London), lxv. p. 373 (1927); also British Patent 278036.

Coming now to the *j-transformation* and the *j^3-transformation*, it will be clear that the latter can be derived from the former by a j^2-transformation, so that we can further limit ourselves to consider the j-transformation only.

As the reactance of a self-inductance and of a capacity depends upon the angular frequency ω of the impressed E.M.F., the j-transformation can be used for one given frequency at a time only, so that when a different frequency is considered, the physical numerical result of the j-transformation is also different. In applying the j-transformation, every positive resistance R in the network, through the multiplication by j, becomes jR, and this has to be interpreted physically as $j\omega L'$, *i. e.* every positive resistance R is transformed into an inductance L′, of amount $L' = R\omega^{-1}$. Similarly, every negative resistance $-R$ has to be replaced by a capacity C′ such that $C' = (\omega R)^{-1}$. Further, every impedance $j\omega L$ becomes $jj\omega L = -\omega L = -R'$, *i. e.* every inductance L has to be replaced by a negative resistance $-R'$ of an amount $R' = (\omega L)^{-1}$. Finally, every capacitive reactance $1/j\omega C$ becomes $j/j\omega C = (\omega C)^{-1}$. This expression

Fig. 2 *a*.

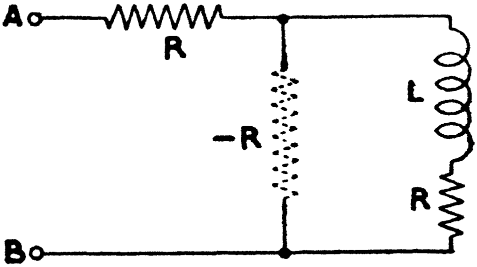
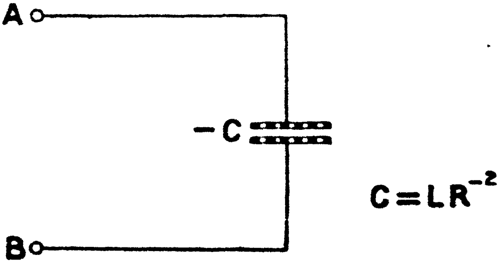


Fig. 2 *b*.



is real and positive; hence every capacity (of value C) has to be replaced by a resistance R′, where $R' = (\omega C)^{-1}$.

It will be clear that in ordinary vectorial representation the j-transformation simply means revolving a vector diagram as a whole over 90°, and then to inquire into the physical meaning of the revolved diagram.

The j-transformation could obviously be extended to transformations such as a $j^{\frac{1}{2}}$-transformation, meaning a rotation over an angle $\pi/4$. However, we will limit ourselves here to integral powers of j only.

Consider, *e.g.*, a series connexion of L, C, $+r_1$, and $-r_2$. Upon this linear system let an E.M.F. be impressed of angular frequency ω. By varying the L or the C, we may bring the system into "*reactance-resonance.*" When, as in a wireless receiver with retroaction, we thereupon make r_2 as near as possible equal to r_1 (*i.e.* adjust the retroaction to the critical point), we do the same thing over again, but only after one j-transformation, and one could say, in a broad sense, that adjusting the total resistance near zero value means bringing the system into "*resistance-resonance.*"

We will now consider some simple a.c. circuits having special properties, and inquire as to what becomes of them after a j-transformation.

Example 1.

Consider fig. 3 *a*, representing a well-known circuit, such as is often used, *e.g.*, in a triode amplifier. This circuit has the property that for resonance, *i. e.* for

$$j\omega L = -\frac{1}{j\omega C}, \quad \ldots \ldots \quad (1)$$

the equivalent impedance Z_{AB} between the points A–B is

$$Z_{AB} = \frac{\frac{L}{C} + r^2}{2r}, \quad \ldots \ldots \quad (2)$$

and is therefore real, *i. e.* a pure resistance. After one j-transformation, fig. 3 *a* is changed into fig. 3 *b*, such that

$$j\omega L = -r_1',$$
$$\frac{1}{j\omega C} = +r_2',$$
$$r = j\omega L'.$$

Thus the condition (1) becomes

$$r_1' = r_2'; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

i. e. in the derived circuit the equality of the moduli of the two resistances corresponds to the resonance condition of the original circuit. And, further, the special property (2) of the original circuit becomes, after our j-transformation,

$$Z'_{A'B'} = \frac{-r_1'r_2' - \omega^2 L'^2}{2j\omega L'} = j\omega L' . \frac{\omega^2 L'^2 + r'^2}{2\omega^2 L'^2}; \quad . \quad (2')$$

Fig. 3 *a.*

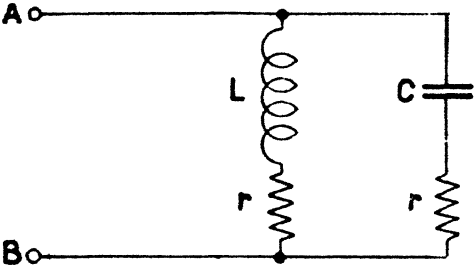
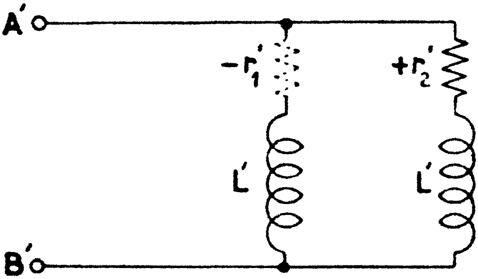


Fig. 3 *b.*



or, in other words, the system of fig. 3 *b* behaves as a pure inductance when the numerical values of $-r_1'$ and r_2' are made equal.

Example 2.

The circuit of fig. 4 *a* has the property that when $j\omega L = -\frac{1}{j\omega C}$, *i. e.* in resonance, the current i_Z through the arbitrary impedance Z is independent of this impedance, viz.

$$i_Z = \frac{E}{j\omega L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

After the application of the j-transformation, fig. 4 *a* becomes fig. 4 *b*. Here, again, the resonance condition of fig. 4 *a* is changed into the equality of the numerical values of the two resistances $-r'$ and r' in fig. 4 *b*. The arbitrary impedance of fig. 4 *a* is transformed into another arbitrary impedance Z′ of fig. 4 *b*. Again (3) changes into

$$i_{Z'}'=-\frac{E}{r}, \quad \dots\dots \quad (3')$$

or in words: the current through Z′ is independent upon the impedance Z′ itself, so that when, instead of E sin ωt, an E.M.F. is applied of arbitrary wave-form, the current through Z′ is an exact image in amplitudes, as well as in phases, of the applied E.M.F.*

Fig. 4 *a*.

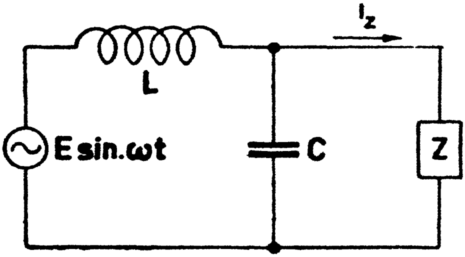
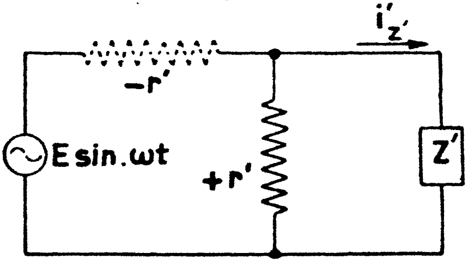


Fig. 4 *b*.



Example 3.

Let a given current i be flowing between the terminals A and B of fig. 5 *a*. It is easy to show that for resonance the P.D. E_Z developing across the impedance Z will be

$$E_Z=\frac{i}{j\omega C},$$

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* This property of fig. 4 *b* was already derived by Bartlett, *l. c.*

and therefore does *not* depend upon the value or constitution of Z.

The *j*-transformation of fig. 5 *a* is given by fig. 5 *b*. If in the latter the negative resistance $-r'$ is numerically made equal to the positive resistance r', then the P.D. developing across the arbitrary impedance Z′ is an exact image of the current i' entering the system, independent of its wave-form.

Fig. 5 *a*.

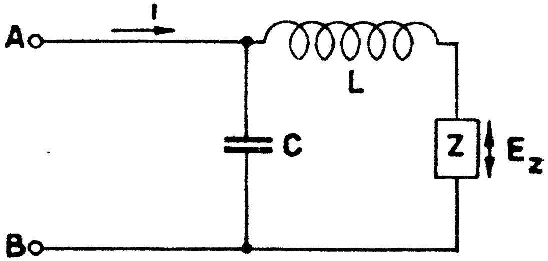
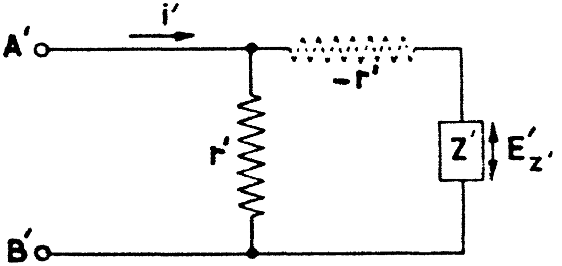


Fig. 5 *b*.



Example 4 (*application to the theory of audition*).

Consider the circuit of fig. 6 *a*. For an impressed E.M.F. of a frequency ω given by

$$\omega^2 = \frac{1}{2LC} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the impedance Z_{AB} between the terminals A B is given by

$$Z_{AB} = j\omega L \cdot \frac{1 - j\omega CR}{1 + j\omega CR} = j\omega L \,.\, e^{-2j\theta}, \quad . \quad . \quad . \quad (5)$$

where

$$\tan\theta = \omega CR. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We therefore see that for the specific frequency given by (4) the modulus of the impedance between the points A and B of fig. 6 *a* does not vary with the value of R. If, thus, an alternating E.M.F. of constant amplitude and of frequency $\omega^2=(2LC)^{-1}$ is maintained between the terminals A–B, the amplitude of the current through the L-branch is unaffected by the value of R, but its phase is. This is a very valuable property for measurement purposes, as we can change the phase over 180° without affecting the amplitude.

When we now apply again the *j*-transformation to the system of fig. 6 *a*, fig. 6 *b* is obtained.

Fig. 6 *a*.

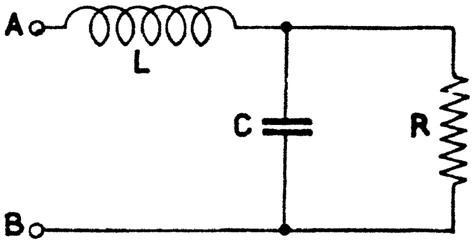
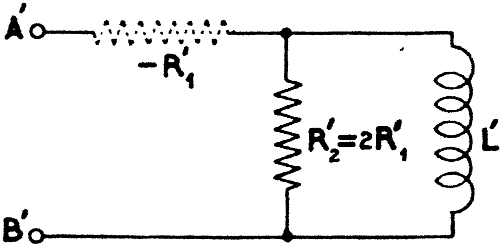


Fig. 6 *b*.



The frequency condition (4) of the former circuit, which can be written

$$j\omega L=\frac{-1}{2j\omega C},$$

now becomes

$$R_2'=2R_1',$$

and does *not* depend upon the frequency, The impedance $Z'_{AB'}$ of fig. 6 *b* now becomes

$$Z'_{A'B'}=-R_1'.\frac{R_2'-j\omega L'}{R_2'+j\omega L'}=-R_1'.e^{-2j\theta'}, \quad . \quad . \quad (5')$$

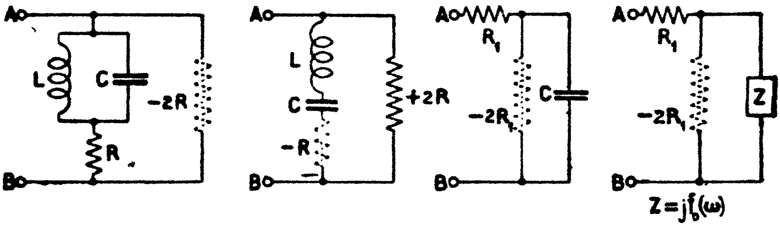
where

$$\tan\theta'=\frac{\omega L'}{R_2'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Our circuit of fig. 6 *b* has therefore the following properties: *the modulus of the impedance of the network between the points* A′ *and* B′ *is the same for all frequencies, and does not depend upon the value of* L′. *The phase, however, does depend upon the value of* L′. *If we therefore apply an E.M.F. of any complicated wave-form to the terminals* A′B′, *all the amplitudes of the various harmonic components of the current entering at* A′ *will be exactly proportional to the corresponding amplitudes of the harmonics of the E.M.F. The phases of the currents, however, are shifted relatively to the phases of the E.M.F. and by an amount depending upon the frequency.*

The limiting cases can be recognized directly. For a very low frequency the L′ branch forms a short circuit in parallel to the R_2' branch. Hence, for a very low frequency the impedance $Z'_{A'B'}$ approaches $-R_1'$. For a very high frequency, on the other hand, the branch L′ (in parallel to the R_2' branch) can be ignored, thus leaving a total impedance $Z'_{A'B'} = -R_1' + R_2' = -R_1' + 2R_1' = +R_1'$. Thus the total possible phase-change is 180°.

Fig. 7.



Several circuits possessing the above properties can be designed. Some other instances are given in fig. 7. (By $Z = jf_0(\omega)$ is meant any impedance consisting of inductances and capacities only.)

For all those circuits having the above property the impedance Z can be expressed as

$$Z = R \cdot \frac{f_e(\omega) - jf_0(\omega)}{f_e(\omega) + jf_0(\omega)} = R \cdot e^{-2j\theta},$$

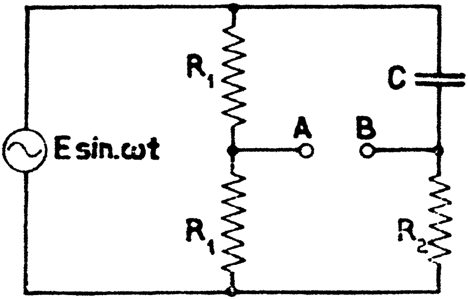
where $f_e(\omega)$ and $f_0(\omega)$ represent an even and an odd function of ω respectively, and where

$$\tan\theta = \frac{f_0(\omega)}{f_e(\omega)},$$

and R represents an ohmic resistance.

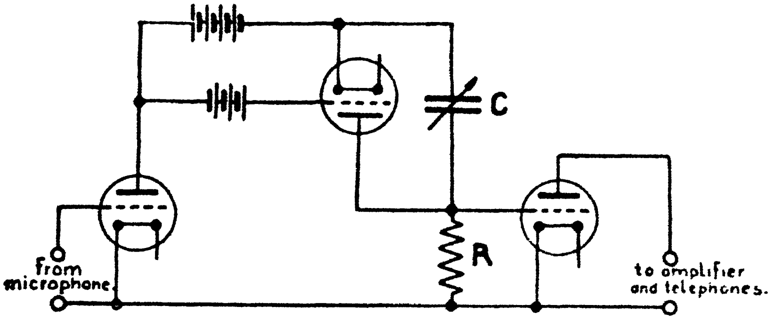
It may be remarked that the circuits considered are quite different from the circuit of fig. 8, described by Möller [*], where the amplitude of the *potential* between A, B is independent of the frequency of the source E sin ωt, while the phase is dependent upon it. However, this is only true as long as the internal resistance of the source E sin ωt is zero, which is difficult to realize in practice with triodes.

Fig. 8.



The property described of leaving the amplitudes of all the composing harmonics untouched but only changing their phases gives us a means of verifying experimentally the well-known acoustical law of Ohm, which states that our ear perceives from a complicated sound the amplitudes of the various components only, but that it cannot recognize the phases of these components. Therefore arbitrary changes made in the phases of the components do not vary our perception of a sound so long as the amplitudes are left unaltered.

Fig. 9.



Now, in order to test this law the circuit of fig. 9 was used.

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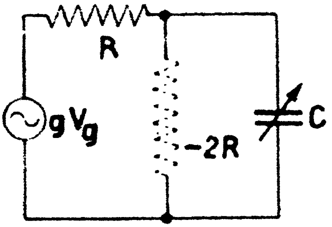
[*] H. G. Möller, 'Schwingungsaufgaben,' p. 43 (Hirzel: Leipzig, 1928).

The first triode acts as an amplifier, while the second triode is used as a dynatron providing the negative resistance. Essentially this circuit is equivalent to the circuit of fig. 10. The current through R represents an exact amplitude image (not phase image) of the grid potential of the first triode. The potential variations over R are the grid potential variations of the third triode.

If the circuit of fig. 9 is properly adjusted, the amplitudes of the various components of the sound spoken in the microphone are not affected by a change of C, but their phases are. If, now, one listened to a loudspeaker connected to the output side of the circuit of fig. 9 while someone else spoke into a microphone set up in a different room, not the slightest difference would be observed after a pronounced change (up to 180° and, with a L inserted in series with the C, even 360°) of the phases of the components. This fact was verified by several persons, so that the above law of Ohm was found true for phase changes up to 360°. Obviously the microphone and the amplifier produced some phase changes already. The fact, however, that the phases of the components could be advanced as well as retarded, makes the above conclusion justified.

Fig. 10.



For *non-periodic* sounds, such, *e.g.*, as the spoken language, phase retardation may be conceived of any amount extending beyond 360°. For instance, at the receiving end of a long telephone cable the time of arrival of the higher speech components may be considerably different from that of the lower components ; this relative retardation may obviously amount to several periods. One cannot expect the ear to be absolutely insensitive to such long relative retardations, and practice with cables bears out this fact plainly.

For *periodic* sounds (such as vowels) and normal amplitudes, however, the above experiments conclusively confirm the classical acoustical law of Ohm, which was also found to be valid for aperiodic sounds (the spoken word) as long as the relative phase retardation between the high and the low components was not greater than 360° of the high components.

Finally, oscillograms were taken of various vowels with and without changes of the relative phases, and the curves for the vowel *a* (the pronunciation in the Dutch language of this vowel is quite near that of the German language) is given in fig. 11 (Pl. VII.) where the lower oscillogram gives the undistorted vowel while the top one is phase-distorted (fundamental frequency = 140 sec.$^{-1}$). It is curious to note that, though the wave-form of the two oscillograms is quite different, there is not the slightest difference audible. This oscillogram was taken by Mr. van der Mark of this laboratory, who in another article describes the technique of these experiments (where also further instances of vowel oscillograms will be found).

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Eindhoven.

LVI. *Concerning the Artificial Preparation of Diamonds.* *By* Dr. Luciano Sesta [*].

[Plate VIII.]

THE problem of the artificial reproduction of diamonds is already an old one, and many experimenters have attacked it with the hope of snatching even this secret away from Nature.

Since 1694–95, in Florence, when Averani and Targioni proved that diamond burning at a temperature of 700–800° C. in an atmosphere of oxygen gives as a product of the combustion *carbonic acid gas* (CO_2), it has by various means been tried to obtain it in the laboratory.

Of all the attempts the most successful was that by Moissan, who, after patient and careful study, succeeded in 1896—obtaining minute examples of artificial diamonds.

The conclusions at which he arrived are as follows [†] :—

(1) Graphite is the variety of carbon stable at a high temperature and under ordinary pressure.

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[*] Communicated by Prof. M. La Rosa.

[†] *Ann. de Chimie et de Phys.* 1896.

(2) Carbon passes from the solid form to the gaseous, that is, it sublimes, and when condensed these vapours give graphite.

(3) Diamonds can only be produced under very great pressure.

Guided by these results, he made his famous experiment with a result that has been retained positive. Later, other experimenters, such as Majorana, Hasslinger, Fischer, and others, undertook these studies following the directions of Moissan, but did not obtain better results.

In 1909, Prof. M. La Rosa, placing under critical examination the experiences of Moissan, saw a newer and clearer, and one might add more elegant, path to follow than that pursued by Moissan and his followers.

Prof. La Rosa has observed first of all that the ultimate deductions of Moissan go beyond the bounds of his experiences ; in fact, he expresses himself thus * :—

". . . . The experiment had only showed that, at the temperature of the voltaic arc and that of the electric furnace carbon sublimes without presenting traces of fusion ; and that the fusion was effected, probably, under the very high pressure resulting from the solidification of cast iron ; hence it was only possible to affirm that carbon does not fuse at the temperature of the electric furnace, and that furthermore it is one of those bodies that assume under great pressure a lower point of fusion. In order to conclude that carbon does not melt under ordinary pressure, it is still necessary to prove that the vapour-pressure of carbon exceeds atmospheric pressure at the temperature of the electric furnace or even at a lower temperature.

"This circumstance has not as yet been ascertained ; in fact, one has rather good reason to maintain that in the voltaic arc and in the electric furnace the tension of carbon vapour is rather small.

"One may therefore hope, with sufficient grounds, that a simple rise in temperature may produce the fusion . . . . ."

According to the above-mentioned deductions, Prof. La Rosa undertook some experimental researches with a view to explaining clearly his idea and consequently showing that the last deductions of Moissan are arbitrary.

By means of the musical arc † the author was able to

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as the relative phase retardation between the high and the low components was not greater than 360° of the high components.

Finally, oscillograms were taken of various vowels with and without changes of the relative phases, and the curves for the vowel *a* (the pronunciation in the Dutch language of this vowel is quite near that of the German language) is given in fig. 11 (Pl. VII.) where the lower oscillogram gives the undistorted vowel while the top one is phase-distorted (fundamental frequency = 140 sec.$^{-1}$). It is curious to note that, though the wave-form of the two oscillograms is quite different, there is not the slightest difference audible. This oscillogram was taken by Mr. van der Mark of this laboratory, who in another article describes the technique of these experiments (where also further instances of vowel oscillograms will be found).

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According to the above-mentioned deductions, Prof. La Rosa undertook some experimental researches with a view to explaining clearly his idea and consequently showing that the last deductions of Moissan are arbitrary.

By means of the musical arc [†] the author was able to realize a higher temperature than that of the continuous arc or of the electric furnace, because under the former conditions the amount of energy liberated within a certain time upon a unity of the gas mass, across which the discharge occurs, is greater than that which is consumed by the voltaic arc; consequently the intermittent arc gives thermic and luminous effects superior to those of the continuous arc. Furthermore, spectroscopic examination allowed the author to note that the *spectrum of the intermittent arc is equal to that of an intense spark* *. It was therefore natural that he should try to attain, by means of the musical arc, the liquid form of carbon.

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Notwithstanding my wish to be concise, it is considered necessary, according to what will be said later, to recall the important experiment which permitted the realization of the liquid phase of carbon.

An ordinary arc with vertical carbons was employed. A tension of 300 volts was used in the main circuit, and a current variable from 1 to 20 amp. The branch circuit had a very small resistance and self-induction, and, furthermore, a capacity of 60 microfarads. The electrodes were immersed in an infusible crucible containing some pure sugar charcoal having a residue of 0·08 per cent. of ash, while the residues of the electrodes amounted to 0·33 per cent. After suitably regulating things, the arc was started. Above the two electrodes that remained *unaltered* were found incrustations of various forms and dimensions. Microscopic examination of these incrustations showed that they consisted mainly of a peripheral part, easily transformable into powder and made up of graphite particles showing the contour of the original charcoal particles, and of a central part lustrous, unctuous and very difficult to powder, and showing under the microscope no trace of the structure of the original charcoal particles. The ash residues left by the graphite thus obtained amounted to 0·05 per cent.

Researches of an experimental nature led the author to conclude that under the said conditions it is futile to think of a cementation of these various particles, due to their impurity, or to the phenomenon of real sublimation of carbon; moreover, repeating the experiment with the continuous arc under similar conditions, even for many hours, does not give the same results: graphite is no longer formed, but only the first example of incrustations above described.

Prof. La Rosa therefore arrives at the conclusion that

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* *Loc. cit.*

the particles of carbon attacked by the intermittent discharge liquefy and weld themselves to the electrodes.

Later, by means of the Joule's effect[*], the liquid form of carbon was attained by exploding a charcoal cylinder and passing across it brusquely a very intense current. Here, too, was confirmed by spectroscopic means the attainment of a greater degree of excitation[†]. This spectral method of excitation was later applied by Anderson to the study of spectra of other metals[‡].

Having thus obtained the liquid form of carbon, it was a question of making it crystallize in order to obtain the diamond; but the stable allotropic form of carbon at high temperatures is graphite, and under previous experimental conditions it was impossible to obtain crystallization, since after the arc was spent, the mass of charcoal remained, for a certain time, incandescent.

It was necessary, consequently, to realize the conditions for fusion and to obtain at the same time a very rapid cooling.

Since the author had noted that the spectrum of the intermittent arc is precisely like that of an intense spark, he substituted this for the arc, in order to obtain the desired conditions.

The spark used in this experiment was charged with a battery of 72 large Leyden jars connected in parallel; the capacity of each was 500 cm. This battery was charged with a Klingelfuss coil of 80 cm. spark started by a medium current of 40 amp.

By this means he obtained particles of crystallized carbon of more or less spherical form, that of cut rubies. They were mainly of a greyish tinge; few were decidedly crystallized, transparent, of high refractive power, and of a density greater than that of methyl iodide (CH_2I_2), (3·2).

A few of the most beautiful particles obtained are reproduced in the following microphotographs (Pl. VIII. figs. 1 & 2) kindly furnished by Prof. La Rosa.

The first of these constitutes a single crystal with curved facets, and is a form composed of two tetrahedra. The second looks like an aggregation of many minute crystals, each of which forms two small pyramids united at their square base, or two tetrahedra. Accurate investigations completely exclude the possibility that these tiny crystals might be due to carborundum (CSi). the only composition that could have led us into error. *The strongest proof was that of combustion.* The above-described particles when *burned in an atmosphere of oxygen left no residues of ash.*

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[*] "Sulla fusione del carbonio per mezzo dell' effetto Joule." *Nuovo Cimento*, ser. 5, xx. (October 1910).

[†] "Sullo spettro della luce che accompagna il riscaldamento elettrico di un bastoncino di carbone." *Nuovo Cimento*, ser. 5, xx. (Nov.–Dec. 1910).

[‡] Anderson, "The Spectrum of Electrically-exploded Wires," Astroph. Journ. li. (1920). Anderson & Smith, "General Characteristics of Electrically-exploded Wires," Astroph. Journ. lxiv. (1926).

All these facts, therefore, allow us to conclude with sufficient assurance that the said particles are minute diamonds. These results were communicated by the author in 1909 to the Seventh International Congress of Applied Chemistry in London, and an account of these interesting experiments is published in 'Transactions of the Faraday Society,' vol. v. pt. 2 (1910).

In a recent article that appeared in 'Nature,' May 19, 1928, was treated the problem of the artificial construction of diamonds. The author, who is known to us as C. H. D., refers to the experiments and results of various experimenters, among whom are Crookes, Parson, and others. He dwells mainly on the works of Mr. Parson and Mr. Duncan, who, as a conclusion to their researches in the field, believe themselves to be justified in affirming that no experimenter has as yet succeeded in producing diamonds in the laboratory, and that all who have heretofore prided themselves in having done so, have deceived themselves, since they have mistaken the crystals of *spinel*, whose properties are very similar to those of the diamond, for the diamond itself. Undoubtedly the works of Prof. La Rosa, to which reference has already been made, have escaped the attention of the above-mentioned authors as well as the author of the article in question.

While realizing the strength of the objections raised against the method of Moissan and his followers, it can be asserted that these are groundless in the case examined.

In fact, with La Rosa's method we have not the *insidious solution* in fused metallic solvents as well as the possible formation of *spinel crystals*, because the particles that might contain traces of magnesia and aluminium are not present. Even when the presence of the crucible composed mainly of silicates is considered, the results obtained will not be weakened, since the crucible as well as the mass of carbon surrounding the attacked region brought about by the discharge remain unaltered at a temperature a little above that of the surrounding atmosphere; furthermore, the crystals obtained burn completely in an atmosphere of oxygen, a result which I think is not obtained by any of the other methods.

These facts are strongly in favour of our thesis; hence the results of the experiments and the accuracy of the method are sure proofs which lead us to withdraw from the ultimate conclusion arrived at by C. H. D. It is believed, nevertheless, that the artificial construction of diamonds from the scientific point of view is no longer an unattainable goal, and that the difficulties that prevent the preparation of large and beautiful diamonds are only technical.

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June 1928.

LVII. *Thermodynamical Properties of the Electron, and Atomic Theory.* By R. D. KLEEMAN, *B.A.*, *D.Sc.*[*]

§ 1. *Introductory Remarks.*

IN a previous paper [†] the writer has made a beginning in the application of thermodynamics to the determination of some of the properties of the electron. In this paper the subject will be considerably extended, and an endeavour made to make it self contained, on account of its interest and importance.

§ 2. *The Equation of State of an Electron Gas.*

Let us consider a mass of electrons at any given density at $T=0$, or at the absolute zero of temperature. Since the electrons repel each other, a positive pressure is associated with the electronic substance under all conditions. Suppose that the substance is allowed to expand adiabatically. External work will be done during the process since the pressure is positive, and the temperature can therefore only decrease. But the temperature cannot fall below $T=0$, and hence does not change, which may be expressed in the important form that the various states corresponding to $T=0$ lie on an adiabatic.

Let us next integrate the well-known thermodynamical equation

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[*] Communicated by the Author.

[†] Phil. Mag. vii. p. 53 (1929).

with respect to v between the limits ∞ and v, where S denotes the entropy of the electronic substance at the volume v, pressure p, and absolute temperature T, giving

$$S_\infty - S_v = \int_v^\infty \left(\frac{\partial p}{\partial T}\right)_v . \partial v. \quad . \quad . \quad . \quad . \quad (2)$$

We may write the equation of state of the substance in the form

$$pv = RT . \phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R is the gas constant, and ϕ a function of v and T. On substituting for p in the preceding equation, it becomes

$$S_\infty - S_v = \int_v^\infty \left(R\phi + RT\left(\frac{\partial \phi}{\partial T}\right)_v\right)\frac{\partial v}{v}. \quad . \quad . \quad (4)$$

At T=0 we have seen that $S_\infty - S_v = 0$, and hence under this condition

$$\int_v^\infty \left(R\phi + RT\left(\frac{\partial \phi}{\partial T}\right)_v\right)\frac{\partial v}{v} = 0. \quad . \quad . \quad . \quad (5)$$

If ϕ may be taken a constant when $v=\infty$, the value of the integral corresponding to the upper limit becomes infinite. The value of the integral corresponding to the lower limit evidently cannot be infinite for all values of v. Hence it follows that when $v=\infty$, ϕ is not a constant but a function of T, which becomes zero when T=0.

Next let us integrate the well-known thermodynamical equation

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad . \quad . \quad . \quad . \quad . \quad (6)$$

with respect to v between the limits ∞ and v, where U denotes internal energy of the substance, which gives an equation which may be written

$$U_\infty - U_v = RT^2\int_v^\infty \left(\frac{\partial \phi}{\partial T}\right)_v . \frac{\partial v}{v}. \quad . \quad . \quad . \quad (7)$$

by means of equation (3). The left-hand side corresponds to the change in internal energy when the volume is increased from v to ∞, and hence it cannot have an infinite value. Since ϕ is a function of T, it follows at once that when $v=\infty$, ϕ is a function of v as well as of T.

Now let us write

$$\phi = \frac{a}{v^\alpha} + \frac{b}{v^\beta} + \cdots \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in this equation, where a, b,... are functions of T and α, β,... constants, which gives

$$U_\infty - U_v = RT^2 \left\{ -\frac{1}{\alpha}\frac{\partial a}{\partial T}\frac{1}{v^\alpha} - \frac{1}{\beta}\frac{\partial b}{\partial T}\frac{1}{v^\beta} - \dots \right\}_v^\infty . \quad . \quad (9)$$

Since the integral corresponding to the upper limit cannot be infinite, it follows that α, β,... must be positive quantities. Therefore, when the electrons are in the perfectly gaseous state (which corresponds to $v = \infty$), we may write

$$pv = RT\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where ξ decreases when v increases, and is less than unity.

§ 3. *The Velocity of an Electron in an Electronic Gas decreases gradually between two Consecutive Collisions, and increases during a Collision.*

Suppose that the velocity of an electron in an electron gas kept at constant volume remains constant between two consecutive collisions. On decreasing the volume of the gas this velocity is decreased, since, according to the previous section, the pressure decreases more rapidly than inversely as the volume.

The velocity thus depends on the length of the free path, which can be indicated, or measured, only by an internal change of the electron. Now suppose that an electron is allowed to pass into a vacuum. We may suppose that it is subjected along its path to a succession of electric fields, which alternately decrease and increase its velocity. Corresponding changes should occur in the electron which register these changes in velocity. It follows therefore that in general the velocity and internal conditions of an electron are related to each other; from which it follows that the velocity of an electron cannot remain constant between two consecutive collisions.

Next, let us suppose that the velocity of an electron increases between two consecutive collisions. The velocity will go on increasing unless reduced by each collision. Suppose that it is reduced to zero. On increasing the volume the pressure of the gas is increased under these conditions—which should not occur, and hence the velocity of an electron cannot increase between two consecutive collisions.

Lastly, suppose that the velocity is decreased between two consecutive collisions. The velocity must then increase during a collision, otherwise it will eventually become zero.

On increasing the volume of the gas the average velocity decreases more rapidly than inversely as the volume, as should be the case.

Hence we have the important result that *the velocity of an electron in an electron gas gradually decreases between two consecutive collisions, and increases during a collision.*

This result will now be obtained in the next section in an entirely different way.

§ 4. *The Effect of the Radiation surrounding an Electron on its Kinetic Energy.*

Electromagnetic radiatiation falling on a substance exerts a pressure upon it depending on the amount absorbed per second ; thus, if p denotes the pressure per cm.^{2} when the radiation is completely absorbed, it will exert the pressure $2p$ when it is completely reflected. An electron may thus be under the action of a number of forces, the resultant effect of which will now be investigated.

Suppose that some of the radiation surrounding the electrons of an electron gas, which is black-body radiation, is removed. The average velocity of the electrons will gradually decrease to correspond to the reduced density, or temperature, of the radiation. This will be brought about by the resultant radiation pressure on each electron acting for a time contrary to its motion.

Next, suppose that some black-body radiation is added to the gas. The effect of the radiation will now for a time be to increase the velocity of the electrons.

Now, the electrons in an electron gas possess velocities of all magnitudes, and a decrease or increase simply changes the distribution of the velocities. Therefore, if the radiation surrounding the electrons of an electron gas in *equilibrium* corresponding to a given temperature has no effect on the velocity of an electron, or if it is in equilibrium with the radiation, it will be in equilibrium with the radiation corresponding to a different temperature. Hence an increase or decrease in the temperature, or density, of the radiation would produce no effect on the velocity of each electron. But since an effect is produced, it indicates that each electron is subjected to a radiation pressure which continually changes its velocity. The direction in which this pressure, or the total force, acts would depend on the direction of motion of the electron ; otherwise no force would be acting. It cannot be in the direction the electron is moving, because its velocity would then continually increase, reasoning along the same lines as in the previous section. Hence the force on the electron acts contrary to the direction of its motion, giving rise to a gradual decrease in its velocity. But since this cannot go on indefinitely, an increase in velocity must take place during each collision. Thus the result of the preceding section may also be obtained from radiation considerations.

It may be noted that equation (10) immediately follows, since under these conditions the pressure of the electron gas will decrease more rapidly than inversely as the volume.

§ 5. *The Effect of the Radiation surrounding an Electron on its Internal Energy.*

Suppose that an electric field is applied to an electron gas whose value is gradually increased to a maximum and then decreased to zero. The average velocity of the electrons is increased as a result, because more work is done on an electron when it moves in the direction the field is acting than when moving in the opposite direction, and hence the temperature will be raised. Hence an alternating electric field applied to an electron gas will gradually raise its temperature.

These considerations apply also to the alternating fields due to the surrounding electromagnetic radiation. Since actually no rise in temperature takes place, it follows that we must look for other forces acting in addition on each electron. Now, the radiation falling on an electron when absorbed in part and stored up gives rise to a somewhat different force acting on it than the one considered. What may happen is shown by considering a plate of a substance placed in a radiation which is perfectly reflected by one side of the plate and absorbed in part by the other side. The energy absorbed by the plate per cm.^{2} if kept stationary is αE, where E denotes the energy per c.c. of the radiation, and α the fraction of the impinging radiation which is absorbed, and which is stored up in the plate in other forms of energy than kinetic energy of the plate as a whole. But radiant energy may be transformed into kinetic energy of the plate as a whole on allowing it to move under the radiation pressure. This pressure on the perfectly reflecting side is 2E and on the other side $E(2-\alpha)$, giving a difference in pressure equal to αE.

Now, in order that the electron may not continually increase in velocity due to the electric fields associated with the radiation, it must absorb radiant energy in the foregoing two ways. Hence the radiation surrounding an electron continually changes its internal energy as well as its kinetic energy. Now, according to Section 4 the effect on the kinetic energy is to continually decrease it, which, however, is compensated by periodical increases taking place during collision. The internal energy will evidently continually increase. But since that cannot go on indefinitely, the internal energy must in part be periodically released. This can only happen during a collision. Hence we obtain the result that *the internal energy of an electron in an electron gas increases between two consecutive collisions, and decreases during a collision.*

§ 6. *The Electric Field surrounding an Electron may undergo an Increase, during which it radiates some of its Internal Energy into Space.*

We have seen in Sections 3 and 4 that the velocity of an electron gradually decreases between two consecutive collisions, and increases during a collision. This increase can only be brought about by a sudden increase in the electric fields of the colliding electrons. The increase in field must begin at the location of each electron and travel outwards with the velocity of light; in other words, a pulse of electric force would be propagated from each electron into space. It may be said to be caused by the electron passing from a state A to a state B. This change in state would be associated with a change in internal energy; evidently a decrease should take place which would appear as radiation. We have seen in the previous section that for other reasons a release of internal energy takes place during a collision.

Furthermore, since force and inertia will be involved in such a change of state, the electron is likely to vibrate about the state B, resulting in a succession of pulses being radiated instead of a single pulse.

In the previous section we have seen that the internal energy is increased between two consecutive collisions, and more or less released during a collision. In this section it is shown how the accumulated internal energy is released, and in what form.

§ 7. *An Electron may radiate in two ways.*

It is well established theoretically and experimentally that

(*a*) An electron radiates when undergoing acceleration, and at the expense of its kinetic energy.

According to the previous section,

(*b*) An electron radiates when undergoing an internal change, and at the expense of its internal energy.

On both cases the radiation is likely to proceed according to the quantum equation

$$E_1 - E_2 = h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

where $E_1 - E_2$ denotes the change in energy, ν the frequency, and h Planck's constant. This equation is known to hold under certain conditions. The energy is radiated as a continuous train of waves, for if it were radiated as two trains with an interval between, each would be radiated according to this equation and hence with different frequencies*.

Since the absorption of internal energy by an electron in an electron gas takes place over its mean free path, it can only be gradual, or *the absorption of radiation by an electron takes place in indefinite amounts.* When the kinetic energy of an electron in an electron gas is increased by the surrounding radiation on increasing its density, *this increase may evidently take place in indefinite amounts.*

§ 8. *The Equilibrium between the Emission and Absorption by the Electrons in an Electron Gas.*

When an electron undergoes an acceleration a for the time ∂t it radiates the energy $\frac{2}{3}\frac{e^2a^2}{c}.\partial t$ into space, according to the process (a) in the preceding section, where c denotes the velocity of light and e the electronic charge. It also radiates the energy $I.\frac{\partial u}{\partial t}.\partial t$, according to the process (b), where u denotes its internal energy and I is an appropriate factor. The energy for these radiations is derived from the surrounding radiation, which exerts a force f on the electron giving rise to an absorption of energy equal to $f.\frac{\partial x}{\partial t}.\partial t$, where ∂x denotes the distance traversed during the time ∂t. An amount of energy $X.\partial t$ is absorbed which does not affect the velocity of the electron but appears as internal energy, where X is an appropriate factor of ∂t. Lastly, the external electric field gives rise to a force F acting on the electron which performs work upon it equal to $F . \frac{\partial x}{\partial t} . \partial t$. When the electron gas is in equilibrium

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* In a subsequent paper it will be shown that a part of the kinetic energy and a part of the internal energy may be radiated as a whole like a part of the internal energy.

$$\frac{2}{3}\frac{ea^2}{c} + I . \frac{\partial u}{\partial t} = f . \frac{\partial x}{\partial t} + F . \frac{\partial x}{\partial t} + X. \quad . \quad . \quad (12)$$

Since

$$a = \frac{F+f}{m}$$

and

$$V = \frac{\partial x}{\partial t},$$

where V denotes the velocity of the electron and m its mass, equation (12) may be written in the general form

$$\psi(F, f, u, V, I, X) = 0. \quad . \quad . \quad . \quad . \quad (13)$$

It can be shown that I and X are functions of F, f, u, and V. The internal energy of an electron cannot increase indefinitely, and hence the change in internal energy $\frac{\partial u}{\partial x}$ will be a function of the internal energy. When the velocity is zero u cannot continually decrease or increase, or u does not change independently under these conditions, and hence $\frac{\partial u}{\partial x}$ is also a function of V. We have seen that when two electrons get sufficiently close to each other the change in internal energy that takes place is attended by a change in external field. Hence we also have that the change is a function of F as well as of f. Finally, we may therefore write

$$\frac{\partial u}{\partial x} = \psi_1(F, f, V, u), \quad . \quad . \quad . \quad . \quad . \quad (14)$$

from which it follows that in general

$$\psi_2(F, f, V, u) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

A comparison of this equation with equation (13) shows that I and X are functions of F, f, u, and V.

Equation (15) expresses the important result that f, F, V, and u are related to each other. An important consequence is that potential energy of attraction may be converted into internal energy. Thus, suppose that an electron initially at rest and at infinite distance from a positive charge moves towards it and becomes stationary at a certain distance, being now not under the action of any force. The work done on the electron by the electric field appears as internal energy of the electron and the positive charge. If this energy be now radiated into space the two charges will again exert a force upon each other according to the well-known laws. Something similar no doubt happens during the collision of two electrons, which we have seen is attended by an increase in their electric fields. This probably means that the field of an electron gradually decreases between two consecutive collisions, and then increases to its previous value during collision. If that were not so, two electrons in an electron gas would never get near to each other when their velocity is small.

Further consequences of the relation will be discussed in the next sections. It should be possible to devise laboratory experiments to test directly the existence of such a relation.

§ 9. *The Formation of Atoms.*

Let us consider what may happen to an electron moving more or less in the direction of a stationary positive charge. The effect of the surrounding radiation, according to Sections 3, 4, and 5, is to continually increase the internal energy of the electron and to decrease its velocity. The effect of the field due to the positive charge will, however, be to increase the velocity. The path described will be of the nature of a spiral. Now, it may happen, according to Sections 3 and 4, that the velocity of the electron after a time becomes zero; it will then, of course, not be under the action of an electric force, which is possible according to equation (15). But it will be under the action of a force when displaced from its position of equilibrium.

Suppose, now, that a second electron is brought near this electrical doublet. The electron of the doublet will now be under the action of a force, because the position it occupies is not the one to which it would have settled down when under the simultaneous action of the positive charge and the extraneous electron in its position.

If the extraneous electron is brought sufficiently near to the doublet, the electron of the doublet might get displaced into a new position of equilibrium at which it would not be under the action of a force, being the position to which it would have settled down under the influence of the positive charge and the extraneous electron.

If the second position of the electron of the doublet corresponds to a smaller value of its internal energy than it possessed in its previous position, the difference during the displacement is radiated into space according to the process (*b*) in Section 7.

The foregoing considerations may be applied to several electrons initially in motion and gradually settling down to stationary positions under the action of a positive charge. The atoms might have been formed in this way, the system gradually changing from a dynamic to a static state *. If two atoms, or an atom and an electron, are brought close to one another, the electrons will be put under constraint, which may result in new positions being occupied and radiations emitted during the process. When the external influences on an atom are removed the displaced electrons which radiated internal energy *gradually* regain their internal energy by absorption from the surrounding radiation (Section 5), and *gradually* slip back to their previous positions during the process. The other displaced electrons are likely to slip back to their positions as soon as the external force is removed, without the displacement in either direction being attended by radiation.

An electron in an atom may *gradually* absorb energy from the surrounding radiation and *gradually* occupy a new position of equilibrium. But this position is likely to be unstable, and the electron might on account of some disturbance or other easily slip back to its previous position. But this process would be *rapid*, since the difference in internal energy between the two positions would be radiated as a continuous train of waves of energy $h\nu$.

§ 10. *Application to the Bohr, Lewis, and Langmuir Atom.*

The previous investigations by the above-mentioned scientists on the spectral and chemical relations of the atom in connexion with their electronic configuration throw some further light on the process of atomic formation as outlined in the previous section. Thus, consider an electron describing a Bohr circular orbit around a positive charge. The electron will gradually slow down and reach a stationary position, according to Sections 3 and 4. In order that its orbit may remain unchanged the electric force F acting on it due to the positive charge will, according to equation (15), gradually decrease to zero when the electron is stationary, and accordingly be given by

$$F=\frac{mV^2}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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* In a subsequent paper another method of formation will be pointed out.

where r denotes the radius of the orbit of the electron. The internal energy of the electron will increase in value equal to the initial kinetic energy, since in the end this is equal to zero, and hence we may write

$$\partial u=\partial(\tfrac{1}{2}mV^2)=mV\,.\,\partial V. \quad . \quad . \quad . \quad (17)$$

The kinetic energy is actually lost by radiation into space, and in doing work against the force f acting contrary to the motion of the electron, which slows it down, according to Section 4. We accordingly have

$$\frac{2}{3}\frac{e^2a^2}{c}\,.\,\partial t+fV\,.\,\partial t=\frac{\partial}{\partial t}(\tfrac{1}{2}mV^2)\partial t$$

or

$$\frac{2}{3}\frac{e^2V^3}{cr^2}+f=m\frac{\partial V}{\partial t}, \quad . \quad . \quad . \quad . \quad (18)$$

since

$$a=\frac{V^2}{r}.$$

The energy, is, however, recovered again through absorption of energy from the surrounding radiation, according to equation (12). In this manner the non-radiating Bohr orbit is explained.

When an electron is transferred from one Bohr orbit to another, the difference in internal energy is radiated into space by the process (*b*) in Section 7. This difference in energy, according to Bohr, consists of the difference between the energies required to move the electron to rest at infinity. From this it follows that the potential energy of an electron becomes internal energy, when through a change in internal energy the electric force acting upon it decreases. This possibility has already been indicated in Section 8. Thus the process of radiation of a Bohr atom is explained.

Similar considerations may be applied to the Sommerfeld elliptical orbits of an electron, and to atoms involving more than one electronic orbit. We have seen that the dynamic atom of Bohr ultimately becomes a static atom; and this may now fulfil all the conditions demanded by the Lewis-Langmuir theory of the static atom in connexion with its various chemical properties. The two rival theories may now be said to be completely reconciled.

It appears from this paper that electromagnetic radiation may spread evenly in space, and may be absorbed by electrons and atoms in indefinite amounts, which appears in the form of internal energy. This energy may be radiated in part or altogether into space, but only as a continuous train of waves whose energy is equal to $h\nu$. With this as basis all radiation phenomena may be explained, of which an outline has been given in this paper. In a subsequent paper this will be further carried out in connexion with radioactivity, ionization, the Compton effect, etc.

Schenectady, N.Y., U.S.A.

LVIII. *On a Supposed Limitation of the Second Law of Thermodynamics.* *By* CHARLES COOLMAN, *Lecturer in Physics in the Agricultural Timiriasev Academy of Moscow*[*].

FAIRBOURNE[†] tried to show theoretically that some considerations of molecular kinetic character lead to the possibility of establishing a transgression of the second Law of Thermodynamics. According to his statement, a funnel-like aperture allows to pass in one direction more molecules than in the other, under pressure, when the mean length of the free path is large as compared with the dimensions of the funnel; this produces a spontaneous difference of pressure at both sides of the funnel.

R. d'E. Atkinson[‡], Witmer[§], and the author[||], the last in a more general way, have proved the error of Fairbourne's conclusions. As I have shown (*l. c.*), this problem, owing to the insufficiency of our knowledge of the laws of reflexion of the molecules from a real wall, cannot be solved from a molecular-kinetic standpoint, in spite of J. W. Fisher's[¶] opinion. Gaede[**], confirming the existence of a minimum conductivity of gases (in the function of pressure), assumed as its only explanation the directing influence of the surface film. He calculated the resulting reciprocal repulsion of two plates (at the same temperature), and showed on a lever-balance (sensibility not indicated), that the effect was, at any rate, a thousand times smaller than the calculated one. From this observation of Gaede we may conclude that a funnel-like aperture might cause a motion of the gas in one preponderating direction.

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[*] Communicated by the Author.

[†] Phil. Mag. (6) xliii. p. 1047 (1922).

[‡] 'Nature,' iii. p. 326 (1923).

[§] Phil. Mag. (6) xlvii. p. 152 (1924).

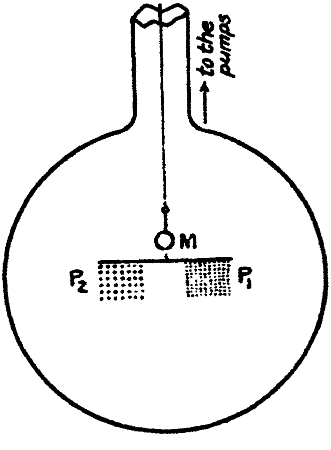
[||] Is sent to the *J. Russ. Ph.-Chem. Soc.*

[¶] Phil. Mag. (6) xlvii. p. 152 (1924).

[**] *Annalen d. Ph.* xli. p. 289 (1913).

On the other hand, J. Kossonogov [*] published an article where he describes a similar phenomenon observed by him in 1920, before Fairbourne's publications. My own careful investigations (*l. c.*) did not confirm the results obtained by him. As the experiments of Kossonogov were conducted under atmospheric pressure and Gaede's method was not sufficiently sensitive, it was interesting to make the following controlling experiments.

Fig. 1.



In the centre of a large bolt-head (diameter about 20 c.) a system was suspended on a quartz thread consisting of a little rod with a mirror M, at the ends of which were attached two thin porous glass plates, P_1 and P_2 (2 c. × 2 c. each), with conical apertures (fig. 1). The porous plates (made by Schott, Jena, 1925) were attached in such a manner that the narrower ends of the conical pores of plate P_1 were turned in the opposite direction to the narrower ends of the pores of the other plate, P_2.

If through each of these conical apertures a greater quantity of molecules flowed in one direction than in the opposite, an easily discoverable rotational moment would be imparted to the system. The diameter of the narrower ends of the pores was 4–5 μ (the mean free path of the molecules of air at 15–18 mm. Hg was the same). The diameter of the larger pores was about 100 μ (corresponding to the pressure of 0·15 mm. Hg). The maximum of declination had to be looked for in these limits. A position when the system was not declined could exist at a very strong rarefaction (according to Gaede the directing action of the surface film disappeared already at 0·001 mm. Hg), or, with some approximation, at the atmospheric pressure. In that case, according to Fairbourne and Kossonogov, the curve would be represented by fig. 2. The period of vibration was about 4 minutes. The moment of inertia was reckoned at 9 C.G.S units. With a scale placed at a distance of 2 m., one division of the scale corresponded to $1 \cdot 4 \,.\, 10^{-6}$ dyn. cm.

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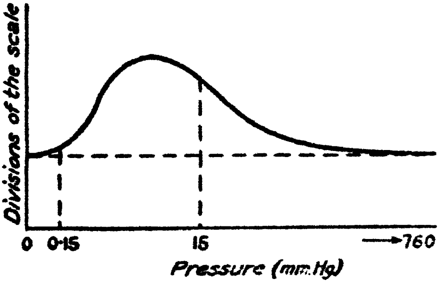
[*] *J. Russ. Ph.-Chem. Soc.* lvi. pp. 25–39 (1924).

Fig. 2.



This, at the maximum of the effect sought for, corresponds for molecules reflected in one direction to the prevalence of one hundred millionth of all molecules fallen. Because of the great sensibility of the method, a good thermal isolation proved to be necessary. It was secured by enveloping the bolt-head in several layers of cotton with interlayers of tin-foil; in front of the window a water cuvette was placed and a scale of total internal reflexion was used.

Three series of observations with a good constancy of the zero in limits from 10^{-7} mm. to 760 mm. Hg showed a complete absence of the effect. An artificial change of temperature in the room showed that the natural variations of temperature could not conceal the effect if such existed.

The same results were obtained with little diaphragm-like wings made of porous plates composed of two layers of gypsum and cement, like those used by Kossonogov. Evidently the directing action of the surface film inferred by Gaede (if it exists) in this case cannot lead to a limitation of the second law because of the unevenness of the surface and perhaps of the oscillations of the surface film itself.

Thus the cases of limitation of the second Law of Thermodynamics pointed out by the above-mentioned authors must be considered theoretically and experimentally as inconsistent.

I take this opportunity for expressing here my profound regret at the recent death of Wladimir Alexandrovitch Michelson (Feb. 27th, 1927), Professor of Physics and head of the Physical Laboratory, who placed at my disposal all facilities for carrying out this work.

Physical Laboratory,
Agricultural Timiriasev Academy,
Moscow, August 1927.

LIX. *Precision Measurements of X-Ray Reflexions from Crystal Powders. The Lattice Constants of Zinc Carbonate, Manganese Carbonate, and Cadmium Oxide.* By J. Brentano, *D.Sc., Lecturer in Physics, Manchester University, and* J. Adamson, *M.Sc., Research Student, Manchester University* [*].

Summary.

Exact determinations of the spacing and of the rhombohedral angle of zinc carbonate and of manganese carbonate, derived from X-ray measurements on crystalline powders, are added to analogous determinations for magnesium carbonate given in a previous paper.

The results are used to verify calculated lattice constants of the carbonate series. Introducing our values, it is found that calculations in which a fixed parameter for the CO_3 group is assumed give good approximation but do not quite agree with the observed data. This indicates that terms characteristic of the various elements have to be considered.

Determinations are made showing the accuracy of the method used. With this method, satisfying a focussing condition, uniformly spaced lines of constant width are obtained and a standardizing substance of great volume absorption is introduced. Some points arising in connexion with its application are discussed.

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[*] Communicated by the Authors.

A determination of the lattice constant of cadmium oxide is made in order to use cadmium oxide as standardizing substance.

1. In a recent paper by one of us and by W. E. Dawson *, exact measurements of the lattice constants of magnesium carbonate were discussed. These measurements introduced an appreciable change in the spacing, bringing magnesium carbonate and calcite, the two extreme members of the isomorphous series of carbonates, into close agreement with respect to calculated values † of their lattice constants derived on the assumptions developed by W. L. Bragg and S. Chapman. The discrepancies of intermediate members are of the same order as the correction introduced in the magnesium carbonate spacing, and it seemed of interest to examine to which extent they might be due to the uncertainty of the lattice measurements. The new determinations were made with a microcrystalline powder, using an X-ray method, and the rhombohedral angle was derived from a consideration of those lattice spacings, the ratios of which were most sensitive to changes in the angle.

2. In the case of a trigonal system, the side a of the elementary cleavage rhomb and the rhombohedral angle α can be calculated by introducing in the relation,

$$d_{hkl}=\frac{a\sqrt{1+2\cos^3\alpha-3\cos^2\alpha}}{\sqrt{(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+hl)(\cos^2\alpha-\cos\alpha)}}, \quad . \quad . \quad . \quad (1)$$

the values of the lattice spacings d_{hkl} which have been obtained from X-ray reflexions (hkl).

Referring more particularly to the determination of the angle α, this can be derived from the ratio of any two spacings, and spacings may be called sensitive for this purpose when they can be combined so that their ratio varies greatly with variation of the angle α. In the case of the isomorphous carbonates of the calcite type, the angle α is about 103°. In these circumstances, as will be seen from equation (1), an appreciable variation in α is only accompanied by a relatively small change in the corresponding values of d_{hkl}. For example, in the case of magnesium

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* J. Brentano & W. E. Dawson, Phil. Mag. (7) iii. p. 411 (1927).

† S. Chapman, J. Topping, and J. Morral, R. Soc. Proc. A, cvi. p. 369 (1924).

carbonate, a change of 0°·1 in the angle α corresponds to a change of 0·0073 in the relative magnitude of the most sensitive spacings. In order therefore to determine the rhombohedral angle, a high degree of accuracy is required in the measurement of the lattice spacings.

We have now measured the lattice constants of zinc carbonate and of manganese carbonate, in order to obtain more exact data for these substances. Since specimens of manganese carbonate are available which permit of exact goniometric measurement, in this case only the value of a was required. We have, however, chosen to determine the rhombohedral angle as well, as a test of the method, and have compared this value derived from the X-ray data with the results obtained by goniometric measurements. Both sets of measurements were carried out on the same crystal specimen.

The method used is based on the general focussing condition for the reflexion from a powder, to which attention has been drawn in an early paper by one of us*, which in the case of a flat layer leads to

$$\frac{\sin\alpha}{\sin\beta}=\frac{a}{b}.$$

α and β are here the angles which the incident and emergent beams respectively make with the surface of the layer, a and b are the distances of the layer from the entrance slit defining the source of the X-ray beam and from the surface recording the reflexions.

The general arrangement of the instrument has been described in a previous paper.

The advantages of this method for making exact measurements depend upon the fact that the reflexions are recorded in such a way as to establish linear relations between the angles of deflexion and the corresponding distances of the lines measured on the film, permitting of direct interpolation between the distances and the angles. Further, when satisfying the focussing condition, symmetrically shaped lines of practically constant width are obtained. These two factors are of great assistance in making absolute measurements of the actual angles of reflexion or in determining the relative position of the lines with respect to a known reference pattern. It must be noted, however, that full symmetry of the lines is only obtained with a thin powder layer which also enables exposures to be taken, using in turn both of its sides, thus eliminating any error due to imperfect centring. In the present case it was decided not to undertake absolute measurements, but to adopt the method which had been used in determining the lattice constants of magnesium carbonate. A standardizing substance was mixed with the powder of the specimen, and a calibration curve prepared in which the observed positions of the standardizing lines are plotted against the angles calculated from its known spacing.

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* J. Brentano, *Arch. Sc. Phys. et Nat.* (5) i. p. 550 (1919); Proc Phys. Soc. London, xxxvii. p. 184 (1925).

The calibration curve is almost a straight line, and the angle of deflexion associated with any point of the film can be obtained with great accuracy. Any systematic errors of the instrument are thus eliminated, and thick layers can be used as long as the absorption in the layer is sufficiently great and the camera sufficiently large to make the asymmetry due to penetration of the X-rays in the layer negligible.

3. The structure of zinc carbonate has been determined by W. L. Bragg[*], using an ionization spectrometer and a single crystal, and by R. W. G. Wyckoff[†], using the Laue method. G. R. Levi and A. Ferrari[‡] have also made a determination of the edge of the elementary cleavage rhomb, using a crystal powder and the Debye method. In no case was a determination of the rhombohedral angle made.

Our evaluation of the rhombohedral angle α respectively of the angle between adjacent faces of the rhomb ϵ was carried out, using the diagram reproduced in the previous paper[§], in which quantities proportional to the logarithms

TABLE I.

L.	Indices.
9·1930	$3\bar{1}\bar{1}$
9·2732	$22\bar{2}$, $2\bar{2}\bar{2}$
9·3080	$31\bar{1}$
9·4238	$31\bar{3}$
9·4725	$40\bar{2}$
9·4948	400
9·5152	$4\bar{2}\bar{2}$
9·6245	$33\bar{3}$, $3\bar{3}\bar{3}$
9·7124	$51\bar{1}$

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[*] W. L. Bragg, Proc. R. Soc. A, lxxxix. p. 468 (1914).

[†] R. W. G. Wyckoff, Amer. Jour. Sc. l. p. 317 (1920).

[‡] Levi & Ferrari, *N. Cim.* xxxiii. p. 516 (1924).

[§] Brentano & Dawson, *l. c.*

of the spacings are introduced, so that differences are substituted for their ratios.

In Table I. we give our experimental values for the glancing angles θ in the form $L = 2 \log \sin \theta$, this being the expression plotted in the diagram.

The value thus obtained for the rhombohedral angle is 103° 27′; it seems therefore unnecessary to suggest any alteration in the usually accepted value 103° 28′ based on a goniometric determination by G. Rose *.

The value for the d_{100} spacing is

$$d_{100} = 5{\cdot}493 \pm 0{\cdot}005 \text{ Å}.$$

as compared with the value $d_{100} = 5{\cdot}44$ Å. obtained by Levi and Ferrari.

The value for the side of the elementary cleavage rhomb becomes

$$a = 5{\cdot}928 \pm 0{\cdot}005 \text{ Å},$$

and the volume of the elementary cleavage rhomb

$$v = 1{\cdot}877 \pm 0{\cdot}015 . 10^{-22} \text{ cm.}^3,$$

giving a density of the pure zinc carbonate of 4·406 g./cm.^{3} This value is lower than the value 4·51 obtained by Levi and Ferrari from their lower value of the d_{100} spacing. Direct density measurements on specimens of zinc carbonate range from 4·30 to 4·45.

4. The structure of manganese carbonate has been determined by W. L. Bragg †, using the ionization spectrometer, and by R. W. G. Wyckoff ‡, using the Laue method.

The results of our measurements are given in Table II.

TABLE II.

L.	Indices.
9·4003	221
9·4475	$32\bar{1}$
9·4956	$42\bar{2}$
9·5413	222
9·5813	$33\bar{1}$
9·6017	$33\bar{3}$, $\overline{333}$
9·6616	500
9·6960	$42\bar{4}$

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* G. Rose, *Pogg. Ann.* lxxxv. p. 132 (1852).

† *L. c.*

‡ *L. c.*

The value obtained for the rhombohedral angle is

$$\alpha = 102^\circ 50'.$$

An accurate goniometric determination of the angle α, for which we are indebted to Mr. H. E. Buckley, M.Sc., made on the specimen from which the powder was prepared, gave the value 102° 50·3′, which agrees with our determination within one minute of arc. These values also agree with the usually accepted value of $\alpha = 102^\circ 50'$ obtained by A. de Schulten *.

For the value of the d_{100} spacing we obtain

$$d_{100} = 5{\cdot}666 \pm 0{\cdot}005 \text{ Å}.$$

The value for the side of the elementary cleavage rhomb becomes

$$a = 6{\cdot}064 \pm 0{\cdot}005 \text{ Å}.,$$

compared with the value $a = 6{\cdot}04$ Å. obtained by Wyckoff, and the volume of the elementary cleavage rhomb

$$v = 2{\cdot}039 \pm 0{\cdot}015 \,.\, 10^{-22} \text{ cm.}^3,$$

leading to a density of 3·747 g./cm.^{3} The values of the direct density determinations on crystal specimens range from 3·47 to 3·76. The variations are mainly due to contamination by other members of the isomorphous series.

5. The determinations of the rhombohedral angles confirm in each case the generally accepted values also for the carbonates of magnesium and of zinc, for which the goniometric determination is more difficult, owing to the imperfections of the crystal and any effect of contamination more likely to occur. It is found more particularly that these values are actually the values of the rhombohedral angles for the crystal specimens for which the determinations of the lattice spacings were carried out. On the other hand, our measurements of the spacing d_{100}, respectively of the side a of the elementary rhombohedron lead to values which in each case differ appreciably from the values obtained in earlier determinations.

In papers by W. L. Bragg and S. Chapman † and by S. Chapman, J. Morral, and J. Topping ‡, the rhombohedral angles of the series of isomorphous carbonates, which includes the carbonates of magnesium, of zinc, and of

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* A. de Schulten, *Bull. Soc. f. Min.* xx. p. 196 (1897).

† W. L. Bragg and S. Chapman, Proc. R. Soc. A, cvi. p. 369 (1924).

‡ S. Chapman, J. Topping, and J. Morrall, Proc. R. Soc. A, cxi. p. 25 (1926).

manganese, are derived by considering the condition of minimum potential energy of the intermolecular electrostatic fields. In these calculations the virtual distance between the C and the O atoms is introduced as a constant parameter for the whole series of carbonates. Using earlier values for the spacing a, the calculated rhombohedral angles show the observed decrease of the angle in passing from the lighter to the heavier carbonates, but do not arrive at a full numerical agreement with the experimental values.

In the earlier paper discussing the accurate values for the lattice constants of magnesium carbonate and giving prominence to the two extreme members of the series, magnesite and calcite, for which exact lattice measurements were available, we have pointed out that very close agreement between the calculated and the observed values could be obtained by a slight reduction of the virtual distance of the C and O atoms. The then resulting discrepancies for other members could possibly be attributed to the uncertainty of the lattice constants.

Introducing our new values for the spacing of zinc carbonate and of manganese carbonate in the calculation, we can compare the resulting rhombohedral angles with the experimental values.

The results are given in Table III. The data previously obtained for magnesium carbonate and those for calcite are added; for the latter obviously no question of accuracy in the determination of the spacing arises.

TABLE III.

	a.	a'.	α.	a.	a'.	α.	α.
Magnesium carbonate ...	5·86	4·61	103° 28′	5·899	4·627	103° 24′	103° 19′
Zinc carbonate	5·90	4·64	103 18	5·928	4·654	103 16	103 28
Manganese carbonate ...	6·10	4·77	102 52	6·064	4·740	102 58	102 50
Calcite	6·38	4·96	102 4	—	—	—	101 55

In the first and second columns the side of the elementary cleavage rhomb a and the distance between adjacent metal atoms a' are given as assumed by Chapman, Topping, and Morral; in the third the values of the rhombohedral angle α so calculated. In the fourth, fifth, and sixth columns are given the corresponding values obtained from our lattice measurements. In the last column are plotted the observed rhombohedral angles.

It will be seen that by using our values for the spacing a', the calculation of the rhombohedral angles leads to values which for magnesium and manganese carbonate are in each case slightly greater than the values actually observed, the difference being 5′ and 8′ respectively. For zinc carbonate, on the other hand, the calculated value is smaller than the observed value, the difference being 12′.

Of the two carbonates for which exact measurements have now been made, manganese carbonate falls thus in line with magnesite and calcite, the difference between the calculated and the observed rhombohedral angles being of the same order and in the same direction in each case, the calculated angle being larger. By a slight reduction of the constant parameter the residual differences could be brought within the limits of the possible experimental errors.

The resulting discrepancy for zinc carbonate would then be increased. This discrepancy is too great to be accounted for by experimental errors. The assumptions on which the calculation is based are thus able to give a remarkably good approximation, but are not sufficient to determine fully the configuration of the crystals of the carbonate series. It will also be seen that an agreement between the calculated and the observed values could not be obtained by introducing a parameter for the effective size of the CO_3 group decreasing regularly with greater atomic weight of the metal. On the basis of the assumptions made in the theory, it would appear that terms for the field distribution characteristic to each metal have to be introduced.

6. The determinations were made on powders, partly owing to the imperfections of the crystals available in the case of magnesium carbonate and of zinc carbonate, partly with the object of using a great number of reflexions for the measurement.

The accuracy of the method used has been discussed in the previous paper, by referring to the agreement between the measurements of the individual lines of magnesium carbonate. It is now indicated in a different way by the agreement of the X-ray determination of the rhombohedral angle of manganese with the result of the direct goniometric measurement, the two values being 102° 50′ and 102° 50·3′ respectively.

A few points may be discussed which have to be considered when making exact measurements from powders.

As has been mentioned above, two essential conditions for an exact evaluation of the X-ray reflexions are to obtain photographic records permitting of a linear interpolation between the distances of the lines measured on the film and the angles of reflexion, and to avoid an asymmetry of the lines due to absorption of the X-rays in the deeper parts of the layer, which introduces errors when strong and weak lines have to be compared. The first condition is satisfied in the particular method used for our measurements. The second condition, to avoid too great a penetration of the X-rays into the crystal powder, can be attained by admixing a standardizing substance of great volume absorption and great volume scattering. By this means the thickness of the layer from which the X-rays are scattered to any appreciable extent can be reduced, and if the standardizing substance presents strong volume scattering, only a small fraction of the reduced volume of the layer, determined by the requirements of sufficient absorption, needs to be occupied by the standardizing substance, which helps to shorten the time of exposure when examining powders constituted of light elements. The reference substance should give a simple pattern, and should be constituted of such elements that their characteristic radiation is not excited by the X-ray radiation used.

7. We have found that nickel oxide in conjunction with Cu $K\alpha$ radiation satisfies the requirements of a standardizing substance, and this was the reason for making a more exact determination of its lattice constant.

In connexion with other work which is in progress, we were led to search for an alternative substance applicable to a range of shorter wave-lengths which would excite the characteristic radiation of nickel. Of a number of substances which we examined for this purpose, cadmium oxide was found most suitable for satisfying the required conditions.

Cadmium oxide can be used for the K radiation of copper, molybdenum, rhodium, and silver; its structure, like the structure of nickel oxide, is of rock-salt type; it gives thus the same pattern of lines, but, owing to the larger spacing, the cadmium-oxide reflexions occur at somewhat smaller angles than the corresponding reflexions of nickel oxide.

A determination of the cadmium oxide spacing by the method just described, with rock-salt as reference substance, gave

$$d_{100} = 4{\cdot}683 \pm 0{\cdot}004\ \text{Å}.$$

Our value is appreciably smaller than the value 4·72 obtained by Davey and Hoffman [*], and obtained again by

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[*] W. P. Davey and E. C. Hoffmann, Phys. Rev. xv. p. 333 (1920).

P. Scherrer[*]. A smaller value, 4·699, had been observed by H. P. Walmsley[†].

The cadmium-oxide powder examined by us showed that a certain part of it consisted of very small particles, so that the lines for the larger angles of deflexion were somewhat blurred. This blurring impairs exact measurements, but only where very great accuracy is required; the two α lines of Cu K radiation, for instance, were quite well separated.

8. In such cases where an exact measurement of a lattice constant is required, and not the determination of a structure, this can often be based on comparative measurements of a group of lines situated within a small angular range in the region of large angles of deflexion. The photographic film can then be placed at a considerable distance from the powder layer, so that the penetration of the rays into the layer has very little effect. In this case it is of advantage to make the distance b of the powder from the photographic film greater than the distance a of the entrance slit from the powder and to satisfy the focussing condition for the ratio a/b chosen. In fact, for a given aperture of the beams, other conditions being the same, the expression for the intensity of the reflected radiation[‡] contains a factor

$$\frac{1}{1+\dfrac{\sin\alpha}{\sin\beta}},$$

which becomes greater when $\alpha<\beta$ or the distance $a<b$; this makes it possible to increase the distance between the photographic film and the powder layer without arriving to unduly long exposures.

From the focussing condition it will be seen that with a given orientation of the powder layer, *i. e.* a given angle of incidence α, the angle β, for which the definition is sharp, varies with b. When satisfying the focussing condition for a film situated at a great distance, for which β and therefore the total angle of deflexion is large, the focussing condition is simultaneously satisfied for a recording surface situated nearer to the powder with a smaller β and thus a smaller angle of deflexion. By disposing two concentric films at different distances, it is thus possible to obtain sharp definition for two different angular ranges at the same time.

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[*] P. Scherrer, *Zeitschr. f. Kryst.* lvii. p. 196 (1922).

[†] H. P. Walmsley, Proc. Phys. Soc. xl. (1927).

[‡] J. Brentano, Phil. Mag. vi. p. 183 (1928).

When determining the lattice constant of cadmium oxide, the distance *a* of the entrance slit from the powder was 13·5 cm., the distance *b* of the main film from the powder was 17·0 cm., and an auxiliary film was interposed at a distance of 5·3 cm. from the axis of rotation of the powder; this film was not protected by a rotating screen, and the lines were more or less blurred outside the region of correct definition.

Only the outer film was used for the actual determinations, but the auxiliary film was convenient for checking the identification of the lines.

In conclusion, we wish to express our thanks to Professor W. L. Bragg, F.R.S., for various facilities, including the use of a transformer obtained by means of a grant of the Royal Society.

Manchester,
Dec. 15th, 1928.

LX. *The Distribution of Electrons in Atoms. By* Lowell M. Alexander, *Ph.D., Associate Professor of Physics, University of Cincinnati* [*].

I.

Stoner [†] makes the assumption that the number of electrons in an atom associated with each sub-level is equal to double the inner quantum number. This gives for the first three levels:—K, 2; L_I, 2; L_{II}, 2; L_{III}, 4; M_I, 2; M_{II}, 2; M_{III}, 4; M_{IV}, 4; M_V, 6. Stoner supports this distribution of electrons by evidence of an indirect nature, *e. g.*, the intensity of X-ray lines, absorption of X-rays, magnetic properties, chemical properties, optical spectra, etc.

II.

In Bohr's picture of the atom, the relation between sub-levels of a group should be similar to the relation between the principal groups. As the K and L groups approach completion, the energy necessary to remove the most lightly bound electron shows an upward trend, reaching maxima in helium and neon, the elements which complete the K and L groups respectively. The outer electron in the next elements (lithium and sodium) is the first electron of the next principal group, and since it is bound on the atom in an orbit of large radius, the energy necessary to remove it is small—in fact, a minimum.

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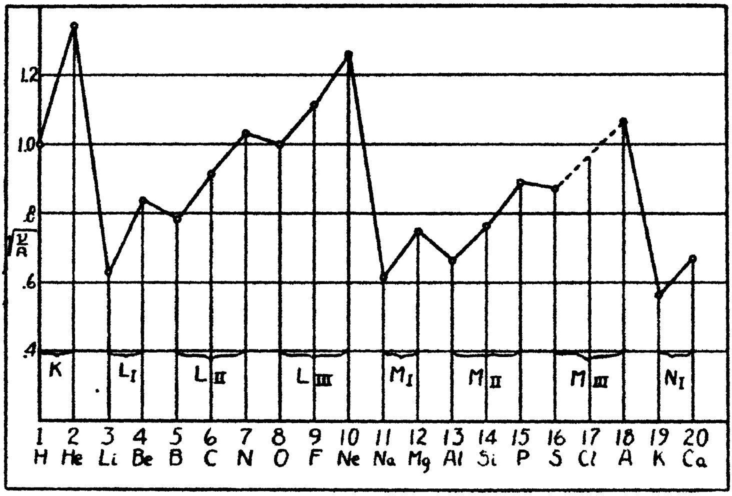
[*] Communicated by the Author.

[†] Stoner, Phil. Mag. xlviii. p. 719 (1924).

We should expect this same phenomenon to occur on a smaller scale as the sub-levels of a particular group are formed. For example, in the formation of the L group one would expect the ionization potential to increase for successive atoms until the L group is complete. The outer electron in the atom of next atomic number is the first electron of the L_{II} sub-level and would be bound on the atom in an orbit of greater radius than the L_I electrons. Thus at this point we might expect a decrease in the ionization potential, although the magnitude of this decrease would be considerably smaller than the corresponding decrease between principal groups. It seems possible in this way to get direct evidence as to the distribution of electrons in sub-levels. The broken line of fig. 1 represents the square root of the energy $\left(\sqrt{\frac{\nu}{R}}\right)$

Fig. 1.



necessary to remove the most lightly bound electron for the elements from H (1) to Ca (20). For brevity, I shall denote X_1 as the energy necessary to remove the most lightly bound electron in the element X. It is seen from the figure that He_1 is greater than H_1, indicating that the second electron in helium is associated with the first to form the K group. Li_1 is considerably smaller than He_1, indicating that the third electron of lithium is not associated with the other two to form a single group, but is the first electron of the L group, indeed, the first electron of the sub-group L_I. As Be_1 is bound on with a greater energy than Li_1, the fourth electron of Be seems to be associated with the third electron to form the completed sub-group L_I. The dip in the curve from Be (4) to B (5) seems to indicate that the outer electron of B (5) forms the beginning of a new sub-group L_{II}. As is seen from the figure this sub-group is completed with N (7), not C (6) as Stoner suggests. O (8) shows the beginning of a new sub-group L_{III}, which is completed at Ne (10). The comparatively large dip between Ne (10) and Na (11) indicates the beginning of a new principal group, the M group. Although the data are incomplete in the range Na (11) to A (18), enough values are known to make it very probable that these eight electrons are bound on in the same way as the electrons from Li (3) to Ne (10). The proposed electron distribution is therefore M_I, 2; M_{II}, 3; M_{III}. 3. The comparatively large dip in the curve between A (18) and K (19) indicates, according to Bohr *, the beginning of the N group, the completion of the M group being made in some unknown manner before atomic number 29. The first eight electrons of the N group proper, beginning at Cu (29) and ending at Kr (36), seem to be bound on with this same distribution, as is shown in fig. 2. This is not entirely conclusive, as the ionization potentials for atomic numbers 32 and 34 are lacking. However, the evidence is perhaps sufficient to propose the distribution N_I, 2; N_{II}, 3; N_{III}. 3. Fig. 2 also shows the beginning of the O group at Ag (47). With the same type of data as exhibited for the N group the indicated distribution is O_I, 2; O_{II}, 3; O_{III}, 3. Fig. 2 shows the beginning of the P group at Au (79). The ionization potential of Bi (83) is given as $8 \pm 0{\cdot}5$ volt, indicating a rather large error of measurement. For reasons of symmetry I propose tentatively the distribution P_I, 2; P_{II}, 3; P_{III}, 3.

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* 'Theory of Spectra and Atomic Constitution,' Bohr.

Table I. shows the data and sources for the first ionization potentials used in plotting figs. 1 and 2.

TABLE I.

At. no.	Term.	ν.	Volts.	Source.
1 H			13·539	(2)
2 He			24·5	(2)
3 Li			5·371	(1)
4 Be			9·50	(1)
5 B			8·34	(1)
6 C			11·3	(1)
7 N			14·494	(1)
8 O			13·565	(1)
9 F			16·9	(1)
10 Ne			21·482	(1)
11 Na	$1\,S$	41448·59		(2)
12 Mg	$1\,{}^1S$	61663·0		(2)
13 Al	$2\,P_1$	48280		(2)
14 Si	${}^3P_0$	64275		(2)
15 P			13·3	(3)
16 S	${}^3P_2$	83554		(2)
18 A			15·4	(2)
19 K	$1\,S$	35005·88		(2)
20 Ca	$1\,{}^1S$	49304·8		(2)
29 Cu	$1\,S$	62305·86		(2)
30 Zn	$1\,{}^1S$	75758·6		(2)
31 Ga	$2\,P_1$	48378		(2)
32 Ge			7·85	(4)
33 As			11·54 ± ·5	(2)
35 Br			10	(3)
36 Kr			13·3 12·7	(2) (2)
37 Rb	$1\,S$	33684·80		(2)
38 Sr	$1\,{}^1S$	45924·31		(2)
47 Ag	$1\,S$	61093·48		(2)
48 Cd	$1\,{}^1S$	72532·8		(2)
49 In	$2\,P_1$	46667		(2)
50 Sn			7·37 ± ·05	(5)
51 Sb			8·5 ± 1·0	(2)
53 I			10·1 ± ·5	(3)
54 X			11·5	(2)
55 Cs	$1\,S$	31406·70		(2)
56 Ba	$1\,{}^1S$	42029·5		(2)
79 Au	$1\,S$	74461		(2)
80 Hg	$1\,{}^1S$	84181·5		(2)
81 Tl	$2\,P_1$	49263		(2)
82 Pb	${}^3P_0$	59821		(2)
83 Bi			8 ± ·5	(2)

(1) Millikan and Bowen, Phil. Mag. iv. p. 561 (1927).
(2) *Anregung von Quantensprüngen durch Stösse*, Franck and Jordan.
(3) 'The Origin of Spectra,' Foote and Mohler.
(4) C. W. Gartlein, Phys. Rev. xxxi. p. 782 (1928).
(5) Green and Loring, Phys. Rev. xxx. p. 574 (1927).

III.

Experimentally 5 absorption limits are known in the M group and 7 in the N group, which would indicate at least 5 sub-levels in the M group and 7 in the N group. As there are 18 electrons in the M group and 32 in the N group, and we have accounted for 8 in each group, we have yet to account for 10 in the M group and 24 in the N group. The formation 2, 3, 3 seems to form a particularly stable set of sub-groups, so that we would not expect the other electrons to intrude on these first three sub-groups as the group is completed. It is proposed tentatively that the M and N groups are completed as shown in Table II. In Tables II. and III. the arrangements of electrons which are not supported by direct evidence are enclosed in brackets.

Fig. 2*.

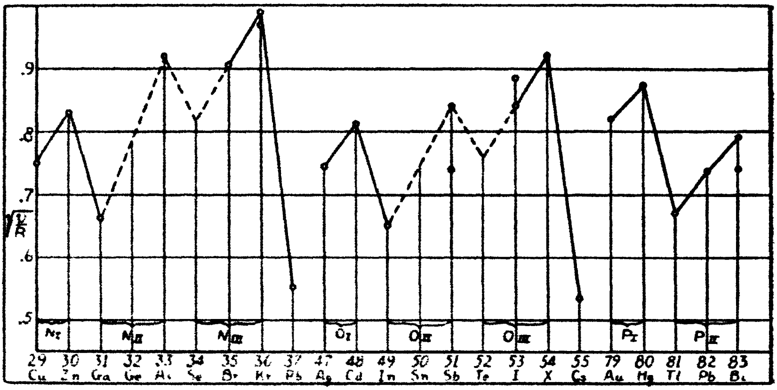

TABLE II.

	Sub-groups.						
	I.	II.	III.	IV.	V.	VI.	VII.
K	2						
L	2	3	3				
M	2	3	3	[5	5]		
N	2	3	3	[5	5	7	7]

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* Since this paper was written I have found references to the ionization potentials of Ge (32) and Sn (50). [See Table I.] The values of $\sqrt{\nu/R}$ are 0·76 for Ge (32) and 0·74 for Sn (50). It is seen that these values lie close to the assumed values shown in fig. 2.

Table III. shows a classification of the electron levels in a few atoms, using Bohr's general scheme together with the distribution of electrons proposed in this paper.

TABLE III.

At. no.	K.	L.			M.					N.							O.					P.		
		I.	II.	III.	I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.	VI.	VII.	I.	II.	III.	IV.	V.	I.	II.	III.
1 H ...	1																							
2 He ...	2																							
3 Li ...	2	1																						
4 Be ...	2	2																						
5 B ...	2	2	1																					
6 C ...	2	2	2																					
7 N ...	2	2	3																					
8 O ...	2	2	3	1																				
9 F ...	2	2	3	2																				
10 Ne ...	2	2	3	3																				
11 Na ...	2	2	3	3	1																			
12 Mg ...	2	2	3	3	2																			
13 Al ...	2	2	3	3	2	1																		
18 A ...	2	2	3	3	2	3	3																	
19 K ...	2	2	3	3	2	3	3			1														
20 Ca . .	2	2	3	3	2	3	3			2														
29 Cu ...	2	2	3	3	2	3	3	[5	5]	1														
30 Zn ...	2	2	3	3	2	3	3	5	5	2														
36 Kr ...	2	2	3	3	2	3	3	5	5	2	3	3												
37 Rb ...	2	2	3	3	2	3	3	5	5	2	3	3					1							
38 Sr ...	2	2	3	3	2	3	3	5	5	2	3	3					2							
47 Ag ...	2	2	3	3	2	3	3	5	5	2	3	3	[5	5]			1							
48 Cd ...	2	2	3	3	2	3	3	5	5	2	3	3	5	5			2							
54 X ...	2	2	3	3	2	3	3	5	5	2	3	3	5	5			2	3	3					
55 Cs ...	2	2	3	3	2	3	3	6	5	2	3	3	5	5			2	3	3			1		
56 Ba ...	2	2	3	3	2	3	3	5	5	2	3	3	5	5			2	3	3			2		
79 Au ...	2	2	3	3	2	3	3	5	5	2	3	3	5	5	[7	7]	2	3	3	[5	5]	1		
80 Hg ...	2	2	3	3	2	3	3	5	5	2	3	3	5	5	7	7	2	3	3	5	5	2		
81 Tl ..	2	2	3	3	2	3	3	5	5	2	3	3	5	5	7	7	2	3	3	5	5	2	1	
86 Em ..	2	2	3	3	2	3	3	5	5	2	3	3	5	5	7	7	2	3	3	5	5	2	3	3

Cincinnati,
March 17th, 1928.

LXI. *Studies in the Formation of Kundt's Tube Dust Figures.*—Parts I. and II. *By* ERIC J. IRONS, *B.Sc.*, *East London College, E.* 1.*

[Plates IX.-XIII.]

Part I.—Dust Figures in General.

§ 1. Introductory and Historical.
§ 2. Experimental Procedure.
§ 3. Description and Consideration of Plates.

Part II.—Formation of Striæ.

§4. Previous Theoretical and Experimental Work.
§5. Present Experimental Work and Conclusions.

PART I.

§ 1. *Introductory and Historical.*

A SEARCH of the more common text-books (1) on sound, and an examination of the most likely papers (2, 3, & 4) failed to reveal any systematic photographic record (5) of the dust figures produced in Kundt's tube. It is the principal object of the present paper to rectify this omission by the aid of an apparatus (already described) which allows such figures to be easily formed.

Kundt (6) performed his original experiments with a four-foot tube of diameter ¾ inch, strewn inside with lycopodium powder. The tube was excited into longitudinal vibration by stroking with a damped woollen cloth, and, when it was closed and suitably clamped, the lycopodium formed figures resembling those of fig. 2 (*a*) (Pl. IX.) of the present paper. Kundt found that on further stroking the tube the antinodes preserved their places, but that the striations were liable to a small change; on stronger excitation the striæ disappeared and the lycopodium gathered at the nodes. If the dust were evenly distributed on the walls, Kundt obtained, after rubbing, *circles* of dust on the *bottom* of the tube around the nodal points of the air column. These he attributed in part to the oscillation of the glass tube itself because of their modified appearance at the nodes of the tube (*i.e.*, the points at which it was clamped). His next experiments were performed in the manner now generally adopted with an independent rod, a metre in length, as a source of vibration. When the length of the air column was suitably adjusted he noted that the nodes in the air were very sharply defined by heaps at the bottom and also by *vertical rings* circling the tube and perpendicular to its axis. In these instances both the end of the metre rod and the stopper in the farther end of the tube determined nodes in the vibrating air, *i.e.*, the length of the column was an integral number of half wave-lengths. If from such a position the stop were moved through a quarter of a wave-length and the experiment repeated then it was found that the nodes preserved their positions with respect to the stop, and that the end of the vibrating rod was situated at an antinode. In these instances the nodal heaps and vertical rings circling the tube were replaced by circles of dust on the bottom of the tube—indicating probably that there was not sufficient energy present to drive the dust to its former positions. Kundt differentiated between the behaviour of lycopodium and of sand in the tube in that firstly, whatever the length of the air column the intensity of the vibration was sufficient to move lycopodium, whereas sand was only affected when the length was an integral number of half wave-lengths; and secondly, the sand striæ were sharper and more regular than those of lycopodium. Iron filings were found to behave in a manner similar to sand. Kundt was not successful in using vapour in place of dust as an indicator. He found that ammonium chloride disappeared at the first stroke of the rod and was precipitated at the nodes in the solid form. He drew the important conclusion that, whatever the form of the figures, the half wave-length of the sound in the tube remained constant.

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* Communicated by Prof. C. H. Lees, F.R.S.

Other papers of note—illustrated by line drawings—are those of Dvořák(7 & 8) in which he offers explanations for many of the phenomena described later in this paper. He also had somewhat narrower tubes than those used in the present work, which were about 4·8 cm. in diameter. He found that when water was placed in the bottom of a tube in which the air was made to resound in the usual manner, it formed a wall across the tube at the antinodes. Assuming that the amplitude of the aerial motion is not small compared with the wave-length, Dvořák shows that there will always be a positive pressure at the nodes, and it is to this pressure that he attributes the motion of the water to the antinodes. He also points out that, owing to friction, the displacement at the middle of the tube must be much greater than at the walls, and suggests that heat is generated at the walls near antinodes giving rise to an increase in pressure at those points. From these considerations he concludes that along the walls of the tube air streams from antinodes to nodes and in the interior from nodes to antinodes. Dvořák's experimental evidence for this and his other conclusions will be considered in § 3; but mention may be made here of a confirmation of this idea made a few years after by the late Lord Rayleigh⁽⁹⁾. He demonstrated mathematically the existence of a current in a Kundt's tube from antinode to node which is limited to an annulus, contiguous to the walls, of thickness 0·293 times the radius of the tube; and a return current from node to antinode occupying the interior and therefore of diameter 1·414 times this quantity. This vortical motion follows as a consequence of postulating viscosity and taking into consideration second order velocity terms; it does not however depend upon the development of heat.

§ 2. *Experimental Procedure.*

The essential features of the apparatus used have already been described⁽¹⁰⁾ and are portrayed in fig. 15 (Pl. XII.)⁽¹¹⁾. As a source of vibration a two-metre rod of brass was employed. This rod, when clamped at its centre and stroked by a resined duster, was capable of emitting both its fundamental and first overtone giving rise to disturbances in the tube having half wave-lengths of c. 19·8 and 6·6 cm. respectively. For most of the work to be described the overtone (generated when the rod is stroked near its centre) was employed, as it was convenient both in regard to its intensity and wave-length. Any trace of the fundamental⁽¹²⁾ (obtained by stroking the rod near its end) was sufficient to destroy the figures obtained with the overtone and *vice versa*, so that the results recorded are not in any way due to the "dual note" property of the rod. It was found unnecessary to take any but rudimentary precautions as to the dryness of the glass tubes which had internal diameters of c. 4·8 cm. The dust to be used was introduced into the tube on a metre scale upon which it had been previously laid in a thin line. The formation of the figures was facilitated by rotating the tube through some 45° to 60° about its axis so that the dust rested on a sloping surface of glass. The distance required between the end of the vibrating rod and the stop for maximum disturbance was determined by trial before a series of photographs was commenced.

The tube containing the figures was photographed *in situ* from above. The stop was removed from the tube to enable the figures to be illuminated from the end and a black⁽¹³⁾ background was placed under the tube, which was completely shielded from extraneous light. In this way the structure of the figures is emphasized by the shadows cast, and reflexions in the tube are eliminated.

§ 3. *Description and Consideration of Plates.*

In the Plates the horizontal arrows point towards the end of the vibrating rod used as a source of sound, and the vertical arrows to the actual position of the end of the vibrating rod in the tube in those instances (figs. 11 & 12, Pl. XI.) where, to illustrate the point at issue, it was necessary to remove the rod during the photographic exposure. In interpreting the figures it should be remembered that they were illuminated, as has already been mentioned, by light travelling in the direction of the horizontal arrows.

The substances used to form figures were cork dust, lycopodium, silver sand, magnetized and demagnetized iron filings, pith dust (14), and *Kieselsäure* (15). With the exceptions of lycopodium and *Kieselsäure* these powders were obtained in a sufficiently divided state by filtering through a copper gauze having some 75 meshes to the inch. The iron filings were demagnetized by heating. All the figures described in this section were obtained with the overtone of half wavelength c. 6·6 cm.

Figs. 1, 2, & 3 (Pl. IX.) show typical results for cork, lycopodium, and sand respectively obtained by a single stroke of the rod (*a*), by two or three hard strokes (*b*), and by continued stroking (*c*). By inclining the tube until its axis was vertical most of the powder fell out, but that which clung to the tube emphasized some essential features when photographed (*vide* (*d*)).

In (*a*) the formation of striæ at the antinodes is shown: these will be considered in detail in Part II. On further excitation these striæ are destroyed and the dust travels towards the *nodes*—most of it going to the node farthest from the vibrating rod—to form, in the case of light powders, a heap and a double ring (16) which encircles the tube (17) ((*c*) and (*d*)). These rings are not so evident with sand, which is more difficult to move. Figs. 3 (*b*) & 3 (*c*) (Pl. IX.) for *sand* resemble Dvořák's drawings for *lycopodium*. He notes that for stronger strokes the limits g and g' separate farther and farther and approach the nodes which, however, they never reach, because as the note gets softer they retreat almost instantaneously to their old positions. This effect has not been found troublesome with lycopodium in the present work, and Dvořák claims to have been more successful in driving g and g' to the nodes by using an extremely small quantity of the seed.

The relative positions of antinodes, rings and nodes may be seen from Table I., which gives an analysis of the observations made in a typical instance.

Table I.

λ/2.	Antinodes.	Nodal Rings.		Nodal Heaps.	λ/2.
	Position of end of vibrating rod......			0·0	
—	(Not measurable.)	6·4		6·5	
	10·1		7·1		6·6
6·6		13·1		13·1	
	16·7		13·6		6·6
6·5		19·8		19·7	
	23·2		20·3		6·5
6·5		26·4		26·2	
	29·7		26·9		6·6
6·5		32·8		32·8	
	36·2		33·5		6·6
6·6		39·3		39·4	
	42·8		40·0		6·6
6·5		46·0		46·0	
	49·3		46·6		6·6
6·6		52·6		52·6	
	55·9		53·2		6·6
				59·2	
	Position of stop			59·2	

In this instance the end of the vibrating rod coincided with a node in the gas column; in general the nearest node is in front of this position (18) (*i. e.*, nearer the stop).

The figures formed by demagnetized and magnetized iron filings are shown in figs. 4 & 5 (Pl. X.) respectively. Striæ corresponding to fig. 4 (*a*) (Pl. X.) did not appear to be formed with magnetized iron filings, which seemed to slip immediately to the bottom of the tube, moving towards (fig. 5 (*a*) (Pl. X.)), and soon surrounding (fig. 5 (*b*) (Pl.X.)) the nodes. A close examination of fig. 5 (*a*) (Pl. X.), however, reveals a certain amount of striation similar to that shown in fig. 4 (*b*) (Pl. X.). The significance of this diversity of behaviour will be discussed in Part II. of this paper. Figs. 4 (*c*) and 4 (*c'*) (Pl. X.) show two further stages of the "closing-in" process.

Figs. 6 (*a*) and 6 (*b*) (Pl. X.) show the initial and a later stage of the process using pith dust.

The figures obtained with *Kieselsäure* are shown in fig. 7 (Pl. X.) (the (*a*), (*b*), and (*c*) correspond to the usual stages).

This substance being very light and finely divided tends to spread in the tube rather than to form into figures. Fig. 7 (*c*) (Pl. X.) illustrates this point, and fig. 7 (*c'*) (Pl. X.) is a deeper print from the same plate to show that the figures are not devoid of structure.

In order to minimize as far as possible the effect of gravitation on the motion of the particles, the figures were next obtained on a plane black lath placed horizontally along the axis of the tube. The results for cork, lycopodium, and sand are shown in figs. 8, 9, and 10 (Pl. XI.) respectively, and in the originals were remarkable for their beauty. The photographs of cork and lycopodium show the results of increasingly strong excitation: nothing more of interest was obtained with sand. As the striæ were irregular and showed a marked tendency to bifurcate or intermingle the device was not subsequently used.

During the progress of this work it became increasingly evident not only that dust was carried from antinode to node but also that it shifted along the tube from the vibrating rod towards the stop. The experiments with cork and lycopodium recorded in figs. 11 and 12 (Pl. XI.) respectively illustrate this observation. A line of dust was introduced into the tube in which the position of the end of the vibrating rod is indicated by a vertical arrow (figs. 11 (*a*) and 12 (*a*)) (Pl. XI.); the stop being towards the right end of the photographs. In the first instance the dust extended from the arrow in both directions; in the second it was confined to the resonant air column. On the first stroke of the rod striæ were formed (figs. 11 (*b*) and 12 (*b*), Pl. XI.), and with a few hard strokes the characteristic figures, already described, were developed in the sound-tube (figs. 11 (*c*) and 12 (*c*), Pl. XI.). The rapidity of progress of the cork dust to the left in fig. 11 (*c*) (Pl. XI.) should be noted: the end of the tube to which it approached was open. From fig. 11 (*d*) (Pl. XI.) it will be seen that further stroking has removed most of the dust from the neighbourhood of the end of the vibrating rod, and that the tongue of dust shown in fig. 11 (*c*) (Pl. XI.) has moved towards the stop to form another node. Figs. 11 (*e*) and 12 (*d*) (Pl. XI.) register further progress, and the lengths of the dust columns here shown should be compared with the corresponding lengths of undisturbed dust in the (*a*) photographs. It was afterwards found that this effect is even more strongly developed by the use of *Kieselsäure*, but it was not obtained with sand. Dvořák observed the existence of this shift, and stated that it was quicker nearer the source of vibration. To verify this statement two 10 cm. lengths of cork dust were placed in a tube with those ends which were nearer the rod coincident with nodes of the air column. After the rod was rubbed the lengths of dust nearer to, and farther from, the rod were found to have increased to 22 and 18 cm. respectively. Dvořák's observation that the dust moves quickest in passing an antinode was confirmed. He found with an open tube that the dust has a tendency to return from the end and remain in the penultimate quarter wave-length, although each stroke of the rod causes it to emerge in a small cloud ; this observation was also substantiated. The shift itself together with its relative magnitudes near the two ends of the air column may be explained in terms of the inequality of intensity which exists between the incident and reflected trains constituting the stationary wave in consequence of losses on reflexion from the end of the tube and the damping effect of the walls.

Fig. 13 (Pl. XII.) shows that the effects so far demonstrated are not localized in any particular part of the tube. Nine half wave-lengths were contained in the sound column, the powder used was cork dust, and the photographs (*a*), (*b*), and (*c*) correspond to stages already described with reference to fig. 1 (Pl. IX.). The shift of dust towards the stop is clearly indicated in fig. 13 (*c*) (Pl. XII.), and by inspection of fig. 13 (*a*) (Pl. XII.) it will be seen that nodes and antinodes are everywhere well defined in the first stage. This result, contrary to Dvořák's observation that striæ were formed everywhere near the vibrating rod although somewhat thicker near the nodes, has also been obtained with much longer resonant columns. It sometimes happens, however, that the antinode figure adjacent to the end of the vibrating rod is not well formed, as, for example, in the instance recorded in Table I.

It remains to discuss the vortical phenomena observed by Dvořák when experimenting with *Kieselsäure*. On excitation this substance was found to rise to the interior of the tube and there to proceed from node to antinode, where it formed a wall across the tube. On the cessation of the source of sound each wall was found to divide into two repelling parts each of which formed a cloud at the nodes with the neighbouring halves from the adjacent loops. An attempt was made by Dvořák to verify the motion described by noting the behaviour of a small rectangle of paper suspended in the tube ; this introduced a disturbing influence, however, which gave rise to anomalous results (19).

Now the motion of *Kieselsäure* in a strongly excited Kundt's tube is not easy to follow with the unaided eye and, in consequence, Part III. of this investigation will be concerned with the results of a cinematographic study (at present in active progress) together with some general conclusions from all the observations.

The photographs of the present paper—notably those for *Kieselsäure*—yield some indication of the existence of a current in the centre of the tube from node to antinode. In fig. 7 (c') (Pl. X.) the antinodes are marked almost as definitely as the nodes and it would appear, both with reference to this figure and also figs. 2 (c) and (d) (Pl. IX.) for lycopodium, that with light powders a cloud occurs near the antinodes which might well be due to the powder falling diffusely from the centre of the tube on the cessation of the exciting vibration, although according to Dvořák the powder falls back to the nodes. It is hoped to settle this point by cinematographic observations, and in Part III. the connexion between this effect and the "line density" and size of the dust particles will also be discussed. There is a slight suggestion of the phenomenon with cork and pith figures but none with sand and iron filings. That these clouds occur slightly towards the "stop" side of the antinodes is ascribed to the general shift towards the stop already mentioned.

Figs. 14 (a) and (b) (Pl. XII.), obtained by the method described in § 5 with cork dust and sand respectively, show a pronounced curvature of the striæ concave towards the nodes. This effect was noted by Dvořák, who stated that it appeared as if two systems of striæ were travelling in opposite directions through one another. Dvořák considered that the curvature was due to the thin layers of dust near the walls of the tube going from antinodes to nodes, while the thicker layers at the bottom of the tube, which were farther removed from the influence of the tube's surface, travelled in the opposite direction. It is notable that these circular striæ are obtained when the excitation of the air is greater than that required to give straight striæ, but not so great as to give the effects shown in "(b)" photographs. (It often happens (*vide* figs. 1 (b) and (c), 3 (b) and (c) (Pl. IX.), and 6 (b) Pl. X.)) that thick circular striæ occur in "(b)" photographs; they appear to be formed as the exciting note dies down.)

It appears probable, both from the manner of its ejection and the fact that the "wall stream" is towards the vibrating rod, that dust expelled from the end of an open tube is carried by the "central stream."

PART II.

§ 4. *Previous Theoretical and Experimental Work.*

The formation of striæ in a Kundt's tube has been explained by König (20) in terms of the hydrodynamical forces between spheres situated in a vibrating fluid. Starting from Kirchhoff's general equations (21) for the motion of two spheres in a perfect fluid, König showed that if R_1 and R_2 be the radii of two spheres separated by a distance r_0, then the components of the forces between them are

$$X = -(\tfrac{3}{2}\pi\rho R_1{}^3 R_2{}^3 \omega_0{}^2/r_0{}^4) \sin\theta(1-5\cos^2\theta),$$

$$Z = -(\tfrac{3}{2}\pi\rho R_1{}^3 R_2{}^3 \omega_0{}^2/r_0{}^4) \cos\theta(3-5\cos^2\theta),$$

ω_0 being the velocity of the stream (considered parallel to the axis of z), ρ the density of the medium, and θ the angle which the line of centres of the spheres makes with the z axis. Further, as he considered the motion to be in the xz plane (*i.e.*, confined to the bottom of the tube), König wrote

$$Y=0.$$

From these equations it follows that, n being an integer,

when $\theta = n\pi$

$$X=0,\ Z=3\pi\rho R_1{}^3 R_2{}^3 \omega_0{}^2/r_0{}^4,$$

and when $\theta = n\frac{\pi}{2}$

$$X=-\tfrac{3}{2}\pi\rho R_1{}^3 R_2{}^3 \omega_0{}^2/r_0{}^4,\ Z=0.$$

Thus it appears that spheres situated in a line parallel to the axis of the tube (*i.e.*, in line with the direction of propagation of the sound disturbance) repel, while those perpendicular to the direction of the tube attract each other. Ignoring other possibilities the *raison d'être* for the formation of striæ is suggested.

Cook (22) attempted to verify these formulæ experimentally and concluded that "A perfect fluid contains forces which are essential but are not sufficient to produce laminæ in the form in which they exist" and that the necessary new forces are "most probably due to the viscosity of the medium." By the microscopical examination of the movements of powder particles, and subsequently of small spheres (23) suspended in a Kundt's tube, Cook found in addition :—

1. That particles with their line of centres *transverse* to the stream lines were maintained in equilibrium when they

were not more than half their diameter apart. (König's theory requires that they should be in contact.)

2. Particles with their line of centres *along* the stream lines and within half their own diameter *approached*, acted as a single system and, like a Rayleigh disk, rotated into a plane perpendicular to the stream lines.

Pointing out that ω_0 varies along the tube when stationary waves are set up so that the arrangement of particles should not be the same in all parts of the tube, Robinson(24) has devised a test of König's theory based upon the measurement of inter-striæ distances. Any one particle in a lamina is in equilibrium under the action of the repulsive forces due to all other particles in the laminæ to either side of it. Summing only the effects of the particles constituting the first laminæ to the right and to the left of the lamina under consideration, Robinson showed that $a_{r\,.\,r+1}/a_{1\,.\,2} = \cos^{4/3}(\frac{1}{2}\pi k/l)$, where $a_{r\,.\,r+1}$ represents the distance between the rth and $(r+1)$th ripples distant k from an antinode and l is the quarter wave-length of the sound disturbance. To test this Robinson performed some experiments with sources of vibration yielding half wave-lengths of 3·63 and 5·03 cm. respectively in the sound tube and succeeded in showing that the distance between the ripples was greater at the antinodes than at the nodes

In a later paper Robinson(25) deduced König's theory on different grounds—though still basing the analysis on Kirchhoff's equations—and extended it to the case where the two spheres do not experience the same velocity. He then found that the square of the mean velocity (ω_0^2) should be replaced by the product of the separate velocities in the formulæ quoted, and finally obtained $a_{r\,.\,r+1}/a_{1\,.\,2} = \cos^{2/3}(\frac{1}{2}\pi k/l)$ as the expression for inter-striæ distances. By experiment the ratio of the distances between the ripples near the nodes and at the antinodes for various combinations of frequency and powder was found to vary between 0·94 and 0·66, and the mean of a number of observations gave 0·78. The ratio of the mean ordinates of the curve $y = b\cos^{2/3}\phi$ for values of the abscissæ corresponding to the positions of the striæ distances measured was also obtained: the process was repeated for the curve $y = b\cos^{4/3}\phi$ and the three sets of ratios were compared. Assuming the striæ to extend 7/9 of the distance from an antinode to a node—as Robinson's observations led him to believe was generally the case—the ratios for the 2/3 and 4/3 power formulæ respectively are 0·76 and 0·56, and on these facts quantitative agreement between the $\cos^{2/3}(\frac{1}{2}\pi k/l)$ formula and the experimental result of 0·78 was claimed.

In a further paper Robinson (26) has shown how ripples may be formed from a powder uniformly distributed on the bottom of a tube by hydrodynamical forces without the intervention of viscous forces. As he remarks, however, this does not preclude the possibility that viscosity may be a factor affecting the formation of ripples.

§ 5. *Present Experimental Work and Conclusions.*

Some observations and measurements on ripples appeared to form the natural sequence to those observations already recorded in the previous paragraphs and accordingly some dozen photographs, with different magnifications, of ripples formed by cork dust, sand, and *Kieselsäure*, in conjunction with notes giving rise to half wave-lengths in the tube of c. 6·6, 7·7, 10·8, and 19·8 cm. respectively were taken. They are shown in figs. 19, 18, 17 (Pl. XIII.), and 16 (Pl. XII.)

For this purpose it was deemed better to use transmitted light and accordingly the figures were photographed from above when illuminated from below by a system of frosted glass electric light bulbs shining through two sheets of opal glass.

The figures were produced from a thin line of dust in the usual manner except that, to minimize the effect of gravitation, the tube was not rotated about its axis, so that the dust lay along the bottom of the tube. So long as the "line density" of the dust be constant its initial distribution is immaterial as, on the completion of a stroke of the exciting rod by a resined cloth, the dust particles must have been established in positions of equilibrium. For the formation of striæ it is necessary that the intensity of the exciting note should be sufficient to agitate the dust, but not so great as to project it towards the nodes.

From an examination of figs. 16 (Pl. XII.), 17, 18, and 19 (Pl. XIII.) it will be seen that thick and thin, or, as it is perhaps preferable to call them, major and minor striations alternate in the dust figures and that these alternations are especially marked in the neighbourhood of the antinodes. So far as the author is aware this effect has not before been noted; it is particularly prominent when the tube is in resonance.

During the process of stroking the striæ may be observed to move slightly backwards and forwards in a direction parallel to the axis of the tube (*vide* Kundt's observation) and in so doing the minor ripples may be drawn into and absorbed by the major and be reformed later. Now according to Robinson's theory of ripple formation (26).

there is always a ripple at an antinode: in practice this is not a general rule and it is suggested that although initially the antinode may be defined by a ripple, yet, due to the backward and forward motion, at the conclusion of a stroke of the rod the ripple may be displaced from the antinodal position.

Despite the presence of minor ripples of which Robinson's theory takes no account, it was thought well to measure the distances between the major striæ of the figures of Pls. XII. and XIII., and accordingly each photographic negative was illuminated from below and the distances read off with a travelling microscope. To keep the relation between $a_{r.r+1}$ and k as general as possible, let us write

$$a_{r.r+1}/a_{1.2} = \cos^n (\tfrac{1}{2}\pi k/l),$$

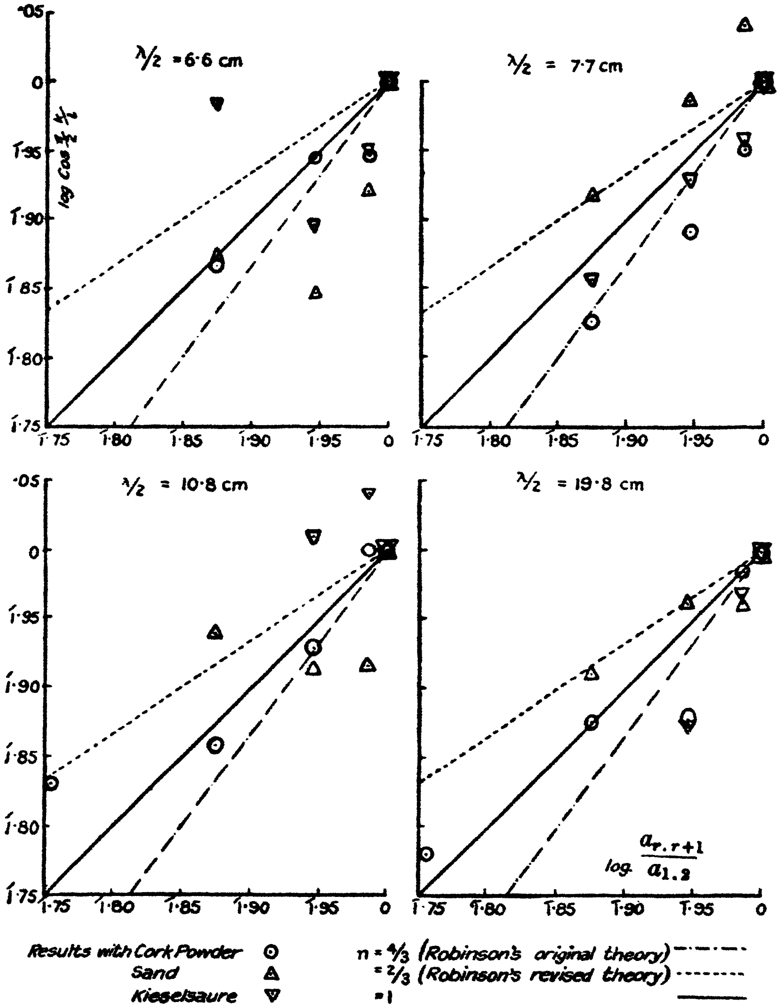
so that on plotting $\log a_{r.r+1}/a_{1.2}$ against $\log \cos (\frac{1}{2}\pi k/l)$ a straight line should result from which the value of n may be obtained (27).

The experimental results were too irregular to justify plotting each value of $\log a_{r.r+1}/a_{1.2}$ against the corresponding value of $\log\cos(\frac{1}{2}\pi k/l)$. In consequence the distance between two nodes was divided into thirteen equal sections, and the mean distance between major striæ in the middle section was taken as $a_{1.2}$. The mean distance between major striæ in the sections to the immediate right and left of the middle section was divided by $a_{1.2}$ and the logarithm of the quotient was plotted against $\log\cos(\frac{1}{2}\pi \,.\, 2/13)$ and so on. The resulting points are shown in fig. 20, to which lines indicating values of n equal to 4/3 (Robinson's original theory), to 2/3 (Robinson's revised theory), and to unity have been added.

Cork dust gives the most consistent results with a value of n equal to unity. In most instances it is almost impossible to assign a numerical value to n, and perhaps the only conclusion justified by these measurements is expressed by saying that, in general, the distance between striæ increases on approaching an antinode. It would perhaps be better to regard this work as failing to support Robinson's theory rather than disproving it. In work of this nature it is almost impossible to ensure that experimental conditions are such as to justify the assumptions upon which the theory is based. Moreover the presence of minor striæ immediately vitiates the theory and it is not easy to see how to introduce a correction for them, as minor striations consisting of single strings of particles have been observed with sand, while in other instances minor striæ comparable in size with major striæ have occurred.

It remains to remark on the fact (noted under § 3) that iron filings appear to form striæ more readily when demagnetized than when magnetized. It is probable that when magnetized the filings form into chains the mutual attractions between the members of which neutralize to some extent the repulsive forces which must exist along the axis of the tube in order that discrete laminæ may be formed. Robinson (28)

Fig. 20.



has attempted quantitative experiments on these lines but without positive results.

Finally, I wish to express my thanks to Prof. C. H. Lees, F.R.S., both for the facilities he has provided and for the interest he has taken in this work.

References and Notes.

(1) Some photographs of somewhat ill-defined striæ are given in Winkelmann's 'Handbuch,' ii. Akustik, p. 198 (1909).

(2) Photographs of striæ formed in a dust tube by an electric discharge have been published, *e. g.*, in a paper by Richmond, Phil. Mag. ser. 6, xviii. p. 771 (1909). (See Pl. XXIV. of that paper).

(3) Some small-scale photographs are given by Hartmann and Trolle, Jour. Sci. Instrs. iv. p. 101 (1927).

(4) The application of the Kundt's tube method to the determination of the velocity of sound in liquids is described by Kundt and Lehmann (*Pogg. Ann.* cliii. p. 1, 1874), and by Dvořák (*Sitz. der Akad. der Wiss. zu Wien*, lxxi. 2, p. 315, 1875). In the former paper striæ are represented in a conventional manner, and the latter paper includes a woodcut (fig. 7) showing striæ formed in water in various circumstances.

(5) This is no doubt due in part to the fact that "Until the last quarter of the 19th century reproductive processes, save as regards line reproduction, can hardly be said to have had an existence." (Encyc. Brit. xxii. p. 408, 11th edition, Article "Process.")

(6) Kundt, *Pogg. Ann.* cxxvii. p. 497 (1866).

(7) Dvořák, *Pogg. Ann.* cliii. p. 102 (1874).

(8) Dvořák, *Pogg. Ann.* clvii. p. 42 (1876).

(9) Rayleigh, Phil. Trans. clxxv. Part I. p. 1 (1884), or Scient. Papers, ii. p. 239. See also 'Sound,' ii. p. 333 (1926).

(10) Irons, Phil. Mag v. p. 580 (1928).

(11) For the purpose of this photograph the rod was pulled back in its support and the stop was advanced.

(12) The fundamental could be eliminated by holding the rod at a point one-sixth of its length from one end during the stroking.

(13) The tube was white enamelled underneath for the purpose of photographing the iron filings.

(14) The use of ground sunflower pith has been recommended by R. V. Cook ('Nature,' cxviii. p. 157, 1926), who with a closed tube (dimensions not stated) obtained "disks that extended completely across the tube and having the same diameter as the inside of the tube." In my experiments ground elder pith, which was more readily available, was used. Its behaviour appeared comparable with that of cork dust. Cook also recommends the use of an organ pipe as a source of vibration; this is not new, and by its use, in conjunction with *Kieselsäure*, Kundt (*Pogg. Ann.* cxxviii. p. 337, 1866) appears to have obtained results similar to those of Cook, leading him to believe that conditions are the same throughout the whole cross-section of the tube.

(15) *Kieselsäure* is prepared by "the action of water upon the tetrahalides of silicon, the gelatinous hydrate obtained yielding silica on ignition as a very light white powder." (Thorpe's Dict. App. Chem. vi. p. 84. Article "Silicon," 1926.) The lightness of this

form of silica, as compared with sand, is due to the air which pervades its interstices.

(16) The ring nearer the stop is usually faint in comparison with the nearer the vibrating rod, but is readily seen when the tube is illuminated in the manner described in § 2.

(17) The sharply-defined nodal heaps of fig. 2 (*c*) would seem to indicate that, where possible, it would be of advantage to revert to the practice of Kundt (*Pogg. Ann.* cxxxv. p. 337, 1868), and determine half wave-lengths by measuring the positions of the centres of these heaps, rather than by noting the positions of corresponding points of striæ figures.

(18) *Vide* Irons, *Ref.* (10).

(19) In a continuously excited tube a hot-wire method might with advantage be employed to investigate the motion, and the author hopes to report the result of such an investigation in a later paper.

(20) König, *Wied. Ann.* xlii. pp. 353, 549 (1891).

(21) Kirchhoff, *Mechanik*, 18 and 19 Vorlesungen, or Robinson, Phil. Mag. xix. p. 476 (1910).

(22) S. R. Cook, Phil. Mag. iii. p. 471 (1902).

(23) See also Cook, Phil. Mag. vi. p. 424 (1903).

(24) Robinson, Phil. Mag. xviii. p. 180 (1909).

(25) Robinson, Phil. Mag. xix. p. 476 (1910).

(26) Robinson, Proc. Phys. Soc. xxv. p. 256 (1913).

(27) When $k = l$, *i. e.*, at a node $\log \cos (\frac{1}{2}\pi k/l)$ is $-\infty$. In practice, however, clear ripples rarely extend farther than $0{\cdot}8\,l$ from an antinode, and over this range the plot proposed is admissible.

(28) Robinson, *Phys. Zeit.* ix. p. 807 (1908).

LXII. *The Effect of a Finite Baffle on the Emission of Sound by a Double Source.* *By* Dr. M. J. O. Strutt *.

Abstract.

In order to calculate numerically the effect of a finite baffle plate on the sound emitted by a double source (representing an oscillating circular plate of dimensions small with respect to the wave-length), the following model is adopted. Two simple sources of equal amplitude and opposite phase are placed in two diametral points of a sphere. The effect of increasing the diameter of this sphere on the circulation of air from one source to the other is taken to be essentially the same as that of a flat baffle plate of finite dimensions. The total energy emitted is calculated as a function of the ratio of the sphere's circumference to the wave-length, and the result is shown in Graph II. The effect of the baffle on the directive properties of the emitter is exhibited in

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* Communicated by the Author.

three graphs as a function of the ratio quoted above. For comparison, the energy emitted by two equal sources of opposite phase without baffling sphere is calculated and shown in Graph VI. This tends to strengthen the hypothesis that the sphere may well represent the effect of a flat baffle.

Introduction.

A FLAT membrane oscillating free in air will only radiate little energy as long as its dimensions are small compared with the wave-length of the sound emitted. This is mainly due to the circulation of air from one side to the other, thus levelling the differences of pressure and destroying the sound-waves. Messrs. Rice and Kellogg[*] pointed out that this effect explains why a good loudspeaker without baffle emits only little energy in the low notes. The use of a baffle-plate diminishes the circulation of air and the levelling of pressure differences, and hence helps to bring out low notes from the loudspeaker. It is clear that an infinite baffle fulfils this aim in the most perfect way, but at the same time shuts off one-half of the loudspeaker.

Practically only finite baffles are used, and so the question arises as to what dimensions should be given to the baffle. From physical reasoning we may expect that enlargement of the baffle beyond a certain critical point, the wave-length being given, will only have little effect, as the conditions for an infinite baffle are practically reached. From considerations of phase, one would expect that this point should be about where the shortest air-path between the front and the back of the loudspeaker equals one-half of the wave-length.

The straightforward way mathematically would be to consider a very oblate spheroid with two equal sources of opposite phase on the ends of the smallest diameter. It appears, however, that spheroidal harmonic analysis has not been carried far enough numerically to effect calculations with this model for any dimensions comparable with the wave-length.

The model adopted therefore consists of a sphere with two equal sources of opposite phase at the ends of one diameter. Numerical calculations may then be carried far enough to cover all interesting points.

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[*] Journ. Am. Inst. El. Eng. p. 982 (1925).

Total Emission of Energy.

If we have a sphere, on which sources of sound are distributed symmetrically with respect to a diameter, the amplitude of velocity on the sphere being given by a function $U(\vartheta)$, where ϑ is the angle with the diameter of symmetry, the velocity potential at any point is given by

$$\psi = -\frac{c^2}{r}\cdot\exp\{ik(dt-r+c)\}\,.\sum_{n=0}^{\infty}\frac{f_n(ikr)}{F_n(ikc)}$$

$$.\,(n+\tfrac{1}{2})\,.\,P_n(\mu)\,.\int_{-1}^{+1}UP_n(\mu)\,d\mu, \quad . \quad . \quad (1)$$

where

ψ = velocity potential,
$k = 2\pi/\lambda$,
λ = wave-length,
c = radius of sphere,
d = velocity of sound,
t = time,
$i = \sqrt{-1}$,
r = distance from centre of sphere,
P_n = Legendre's function of order n,
$\mu = \cos\vartheta$.

For large values of r we have $f_n(ikr)=1$. The functions $F_n(ix)$ are given by

$$F_1(ix)=2+i\left(x-\frac{2}{x}\right),$$

$$F_3(ix)=7-\frac{60}{x^2}+i\left(x-\frac{27}{x}+\frac{60}{x^3}\right),$$

$$F_5(ix)=16-\frac{735}{x^2}+\frac{5670}{x^4}+i\left(x-\frac{135}{x}+\frac{2625}{x^3}-\frac{5670}{x^5}\right),$$

$$F_7(ix)=29-\frac{4284}{x^2}+\frac{148995}{x^4}-\frac{1081080}{x^6}$$

$$+i\left(x-\frac{434}{x}+\frac{29925}{x^3}-\frac{509355}{x^5}+\frac{1081080}{x^7}\right).$$

As will appear shortly, only odd indices are needed. In our model U is only sensible for $\mu=\pm 1$, and in these points U has equal values of opposite sign. Hence the integral in equation (1) gives zero for any even n, so that we may write

$$\psi = -\frac{1}{\pi r}\exp\{ik(dt-r+c)\}\,.\sum_{n=1,3,5\ldots}\frac{f_n(ikr)}{F_n(ikc)}\,.\,(n+\tfrac{1}{2})\,.\,P_n(\mu)\,.\,Q, \quad . \quad . \quad . \quad . \qquad (2)$$

where Q represents the product of the given velocity of air and the element of surface integrated over the surface of *one* source.

From (2) we may readily calculate the energy emitted by our model and find

$$W = \rho\frac{k^2\,dt}{2\pi}\,.\,Q^2\,.\,2e. \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

(ρ density of air),

where

$$e = \sum_{n=1,3,5\ldots}\frac{n+\frac{1}{2}}{\alpha_n^2+\beta_n^2} \quad \text{and} \quad F_n(ikc) = \alpha_n + i\beta_n. \quad . \qquad (4)$$

So e is a measure for the energy emitted, with frequency and Q kept constant. Numerically we find from (4):

kc	·5	·8	1·0	1·3	1·5	2·0	...	...
e	·0925	·218	·300	·369	·372	·344	...	...
kc	2·2	2·5	3·0	3·5	4·0	4·5	5·0	10
e	·336	·349	·407	·423	·404	·411	·443	·461

All calculations, starting with the tabulation of the functions F_n, have been carried out with a slide-rule of 25 cm., so that the last figure of the result may be wrong by some units. The tabulated values of the functions $F_n = \alpha_n + i\beta_n$ are given in the appendix. For $kc = {\cdot}5$, 1·0, 2·0, and 10 values given by Rayleigh [*] have been used.

It is desirable to know the value of e for an infinite baffle ($kc \to \infty$). In this case we have twice the configuration of a simple source close to an infinite plate. Hence, in our notation, the energy emitted is

$$W = 2\,.\,\rho\frac{k^2\,dt}{4\pi}\,.\,Q^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

By comparing (3) and (5) we easily deduce that the value of e for $kc \to \infty$ must be one-half.

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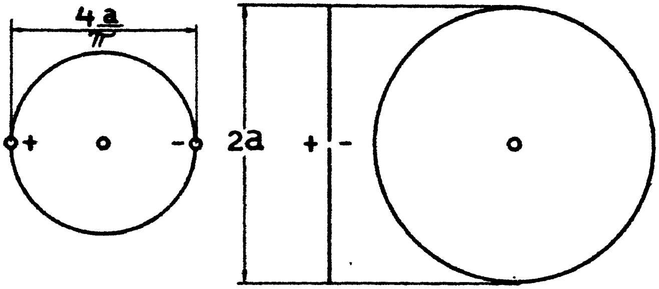
[*] 'Theory of Sound,' ii. p. 255 (2nd ed.).

Here c is the radius of the sphere and

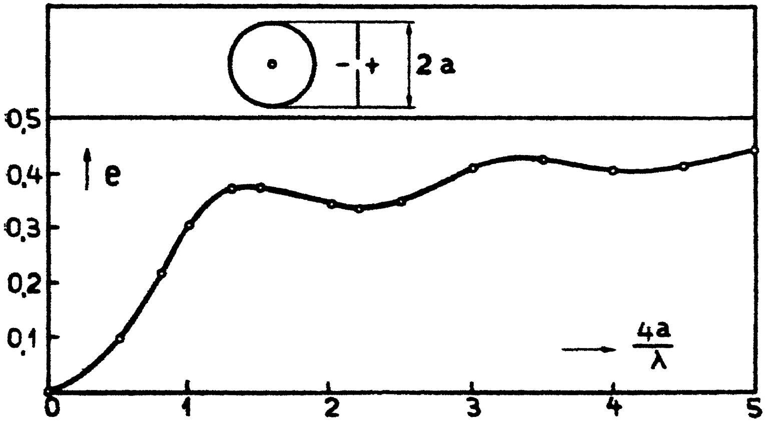
$$kc = \frac{2\pi}{\lambda} c.$$

We may expect that the shortest paths of sound in the spherical model may be compared with the shortest path

Graph I.



Graph II.



in the case of a flat baffle in the shape of a circular ring. Hence we should take (Graph I.)

$$kc = \frac{2\pi c}{\lambda} = \frac{4a}{\lambda},$$

where a is the radius of the outer circumference of the baffle. From the above table Graph II. has been drawn, giving e as a function of $4a/\lambda$.

It appears that enlargement of a beyond $a \sim \lambda/4$ gives only little effect. This may be called the saturation value of a indicated in the introduction. If $4a/\lambda = 1$, the shortest path from the front to the back of the vibrating membrane, or in our model from the positive source to the negative one, equals one-half of the wave-length, bearing out what would be expected from phase considerations. It is interesting to see from Graph II. that the value of e with $a = \lambda/4$ is still only 60 per cent. of the value for an infinite baffle. Increasing $4a/\lambda$ to 3 brings e to about 80 per cent. of the final value. The first oscillation in the e-curve is about 10 per cent. of the e-value at that point, and so may be detected by a careful measurement.

Directive Properties.

A flat circular membrane, oscillating as a whole, situated in an infinite baffle, has remarkable directive properties if the dimensions become larger than the wave-length, the radiation diagrams produced being wholly equal to the well-known diffraction patterns obtained with a circular aperture. When the dimensions of the membrane are small compared with the wave-length, all of the directive properties are lost as long as the baffle is infinite, the radiation diagram being a semicircle. Here a finite baffle may step in and cause directive properties, as soon as the dimensions of the baffle are comparable with the wave-length. But instead of a sharp beam with some small companions, as in the case considered first, we can only produce some rather broad beams of similar size.

In order to obtain the radiation diagrams for various values of $4a/\lambda$, we must go back to equation (2). Let F and G be given by

$$\mathrm{F} + i\mathrm{G} = \sum_{n=1,3,5\ldots} \frac{n+\frac{1}{2}}{\mathrm{F}_n(ikc)} \mathrm{P}_n(\mu), \quad . \quad . \quad . \quad . \quad (6)$$

then

$$\mathrm{I} = \mathrm{F}^2 + \mathrm{G}^2$$

is a measure for the intensity in the direction $\mu = \cos \vartheta$ considered. I have calculated F and G from (6) for various values of μ, and for $kc = 4a/\lambda = \frac{1}{2}$; 1; 2. In these calculations use has been made of figures given by Rayleigh. The result is exhibited in Table I.:—

TABLE I.

$4a/\lambda=\frac{1}{2}$.

$\vartheta=\cos^{-1}\mu$.	0°.	15°.	30°.	45°.	60°.
F …………	·1811	·1754	·1589	·1312	·0928
G …………	·3168	·3069	·2780	·2292	·1643
$F^2+G^2=I$.	·1331	·1250	·1024	·0697	·0356

$4a/\lambda=1$.

$\vartheta=\cos^{-1}\mu$.	0°.	15°.	30°.	45°.	60°.
F …………	·5540	·5428	·5046	·4324	·3206
G …………	·2705	·2662	·2501	·2171	·1631
$F^2+G^2=I$.	·3790	·3660	·3173	·2346	·1297

$4a/\lambda=2$.

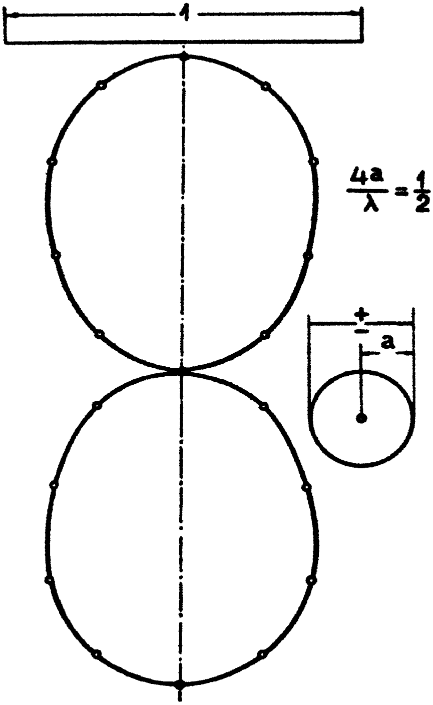
$\vartheta=\cos^{-1}\mu$.	0°.	15°.	30°.	45°.	60°.	75°.
F………………	·2737	·3119	·4011	·4772	·4552	·2847
$-$G……………	·1359	·1554	·2117	·2388	·2275	·1419
$F^2+G^2=I$……	·0934	·1214	·2065	·2806	·2593	·1016

The calculations have been carried out with the slide-rule of 25 cm., and so the last figure is uncertain.

From Table I. the radiation diagrams (Graphs III., IV., and V.) have been drawn. If $4a/\lambda=\frac{1}{2}$, the departure from a cosine law, which holds exactly in the limiting case ($4a/\lambda=0$), is not very marked. The intensity, being zero in our measure for $4a/\lambda=0$, is still weak. Increasing $4a/\lambda$ to 1 brings the intensity to a much higher value, at the same time making the departure from the cosine law of radiation conspicuous. For $4a/\lambda=2$ two distinct beams have been formed. We may expect that with still greater baffles more distinct beams will occur, the total aspect of the diagrams, however, becoming nearly a circle for large values of $4a/\lambda$.

From Table I. we may readily calculate the phase-angle $\theta = \tan^{-1}(G/F)$ for different directions, which, however, varies little with ϑ.

Graph III.

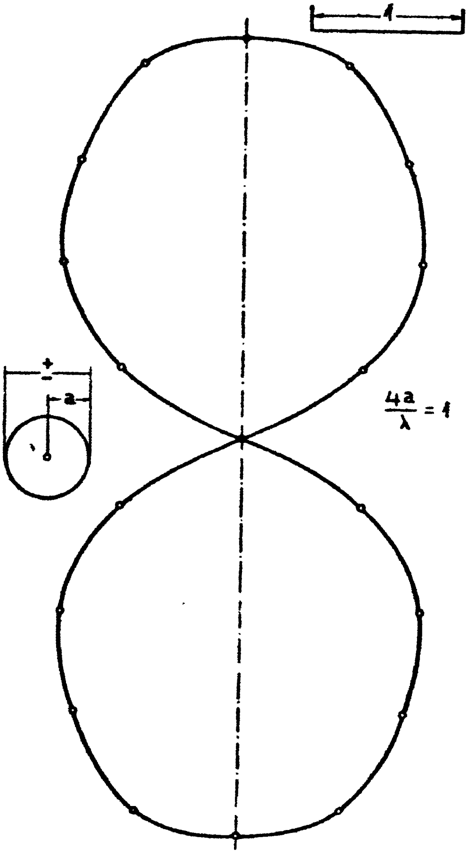


Graphs III., IV., and V. represent the *intensity* of sound in different directions as influenced by the enlargement of the baffle, and should be rotated about the vertical axis.

Radiation by Two Separate Simple Sources without Baffling Sphere.

The supposition that our spherical model might fairly well represent the effect of a flat baffle, is based on the assumption that the preponderant factor in the emission of energy is the shortest air-path between the front and the back of the vibrating membrane. If this is right, the effect of increasing the distance between two simple sources of equal amplitude and opposite phase must be essentially the same as that of a baffle, the distance between the sources being the important parameter. Now, by an elementary

Graph IV.



calculation we find for the velocity potential of two such sources of strength Q each :

$$\psi = -\frac{Q}{2\pi r} \cdot \exp\{ik(dt - r)\} \cdot \cos\left(\frac{kd_1}{2}\cos\vartheta\right)$$

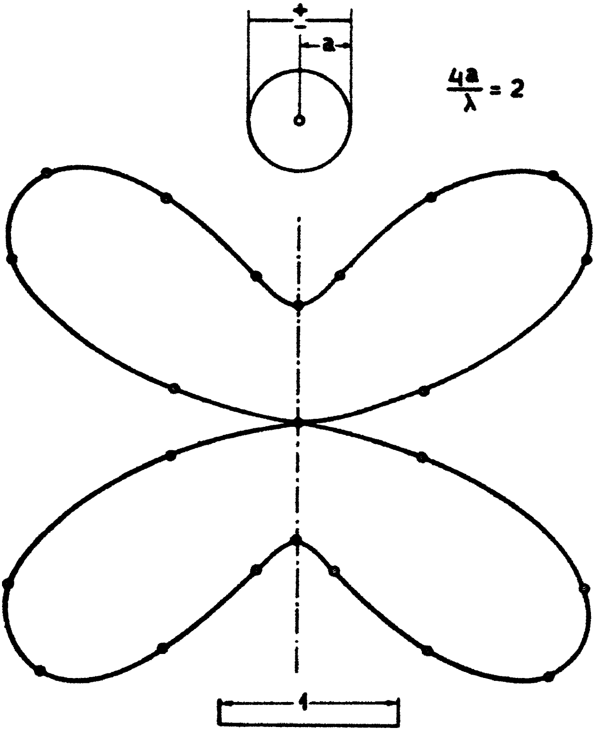
(d_1 distance between sources).

This expression holds good only for large r, r being the distance from the centre of the line joining the sources. From the above formula we may find the total energy emitted:

$$W=\rho\frac{k^2\,dt}{2\pi}Q^2\left(1-\frac{1}{kd_1}\sin kd_1\right)$$

$$=\rho\frac{k^2\,dt}{2\pi}Q^2\,.\,E.$$

Graph V.



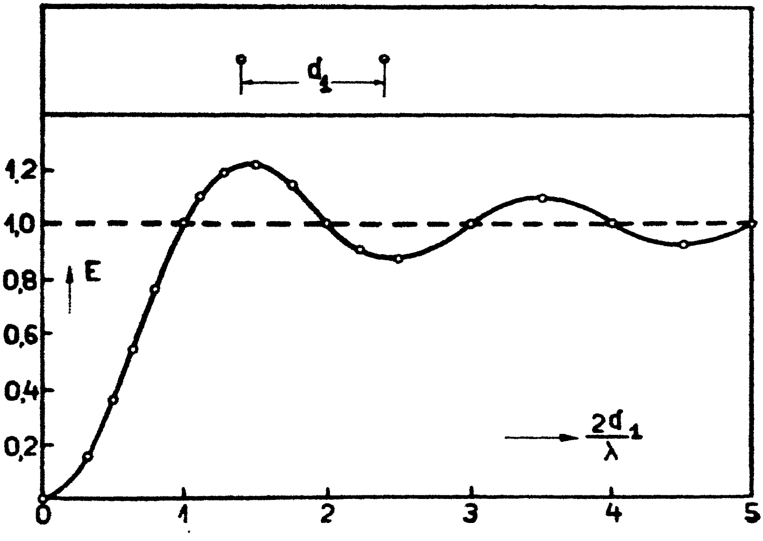
Graphs III., IV., and V. represent the *intensity* of sound in different directions as influenced by the enlargement of the baffle, and should be rotated about the vertical axis.

The last factor contains the influence of the distance d_1 between the sources. It gives, as a function of kd_1, an oscillating curve, which, however, differs only slightly from 1 for values of kd_1 larger than $\pi/2$, or

$$d_1=\frac{\lambda}{2}.$$

We find again, as with the spherical model described first, that the energy emitted does not increase sensibly beyond a certain point, this saturation value of d_1 being equal to one-half of the wave-length. With our spherical model we found that the saturation value of half the sphere's circumference, being the shortest air-path between the sources, is equal to about one-half of the wave-length. Thus the assumption that the shortest air-path is the only preponderant factor in the problem is confirmed by comparison of the two cases considered, and we may expect that our spherical model is a fairly good representative of a flat baffle.

Graph VI.



APPENDIX.

In calculations of the kind carried out above, a table of the functions

$$F_n(ix) = \alpha_n + i\beta_n$$

is of great use. As no such table has come to my knowledge, I thought it well to give the values which I calculated for the above purpose in Table II. Rayleigh gave the values of F_0 to F_5 for $x=\frac{1}{2}$, and of F_0 to F_7 for $x=1$ and $x=2$. The last figure in the table is uncertain, a slide-rule of 25 cm. having been used.

TABLE II.

x ...	·5	0·8	1·3	1·5	2·0	2·2	2·5	3·0	3·5	4·0	4·5	5·0
α_1...	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00	2·00
β_1...	−3·50	−1·70	·240	·169	1·00	1·29	1·70	2·33	2·93	3·50	4·01	4·60
α_3...	...	...	...	...	−8·00	−5·40	−2·60	·33	2·10	3·25	4·04	4·60
β_3...	...	...	...	...	4·00	−4·44	−4·46	−3·78	−2·81	−1·82	−·84	·08
α_5...	...	...	...	...	...	...	...	4·30	−6·20	−7·80	−6·50	−4·31
β_5...	...	...	...	...	...	...	...	32·0	15·5	5·70	·22	−2·80
α_7...	...	...	...	...	...	...	...	...	...	...	...	27·1
β_7...	...	...	...	...	...	...	...	...	...	...	...	8·00

Physical Laboratory of
Philips's Glowlamp Works Ltd.,
Eindhoven, Holland.
October 1928.

LXIII. *A Dynamical Method for the Determination of Young's Modulus by Bending.* *By* KAMTA PROSAD, *M.Sc.(Cal.), B.A.(Cantab.)*[*].

Introduction.

THE purpose of this communication is to describe a method tor the determination of Young's modulus of materials in the shape of bars by dynamical bending.

Theory.

It has been shown by the late Lord Rayleigh[†] that for lateral vibration of bars the frequency is given by

$$\nu = \frac{k \, . \, b}{\pi 2 L^2} \, . \, m^2,$$

where

k = radius of gyration of the section about an axis perpendicular to the plane of bending.

b = velocity depending on the material of which the bar is made.

m = an abstract number depending on the mode of vibration.

L = length of the vibrating portion of the bar fixed at one end and free at the other.

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[*] Communicated by the Author.

[†] 'Theory of Sound,' 2nd ed. i. p. 273

If the section of the bar be rectangular and of thickness t in the plane of vibration, then $k^2 = \frac{1}{12}t^2$ and b is nothing else than the velocity of sound in the material of the bar, and is given by

$$b = \sqrt{\frac{q}{\rho}},$$

where q is the Young's modulus and ρ the density of the material of the bar.

We thus have

$$\nu = \frac{\sqrt{q} \, . \, t}{\sqrt{\rho} \, . \, \sqrt{12} \, . \, 2\pi L^2} \, . \, m^2$$

or

$$\nu^2 = \frac{t^2 \, . \, m^4}{48\pi^2 L^4} \, . \, \frac{q}{\rho},$$

which can be put in the form $y = A \, . \, x$, representing a straight line through the origin by putting

$$y = \nu^2,$$

$$x = \frac{1}{L^4},$$

and

$$A = \frac{t^2 \, . \, m^4}{48\pi^2} \, . \, \frac{q}{\rho}.$$

For the gravest mode of vibration *, $m = 1{\cdot}8751$. Thus, by plotting ν^2 against $\frac{1}{L^4}$ a straight line would be obtained, and the tangent of the angle which this straight line makes with the axis of $\frac{1}{L^4}$ would be given by

$$\tan\theta = A = \frac{q}{\rho} \, . \, \frac{t^2 \, . \, m^4}{48\pi^2}.$$

As t and m are known, $\frac{q}{\rho}$ could be determined, and knowing ρ for the bar, we can calculate q.

The author is not aware if this method has been previously used for the determination of Young's modulus. Possibly one reason for not making use of the above simple relation might have been the uncertain end-correction to be made to

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* *Loc. cit.* pp. 278–288.

the vibrating portion of the bar, as the effect of any attachment to it for the purpose of determining its frequency is to alter its mode of vibration.

End-correction.

The method adopted here for the purpose of making end-correction is to assume that the effect of adding any load at the free end of the bar is to effectively lengthen it, and will be clear from what follows.

For, let the vibrating length of the bar be l_1 with the end-oad on, and its frequency ν_1. Then ν_1 is really the frequency of an unloaded bar of length $(l_1+\delta)$, where δ is the end-correction.

The frequency according to the relation given before for an unloaded bar must be given by

$$\nu_1=\frac{t\,.\,\sqrt{q}}{2\pi\sqrt{12}\,.\,\sqrt{\rho}}\cdot\frac{1}{(l_1+\delta)^2}\cdot m^2.$$

For another length l_2 of the bar, but with the same end-load,

$$\nu_2=\frac{t\,.\,\sqrt{q}}{2\pi\sqrt{12}\,.\,\sqrt{\rho}}\,\frac{1}{(l_2+\delta)^2}\cdot m^2$$

or

$$\frac{\nu_1}{\nu_2}=\frac{(l_2+\delta)^2}{(l_1+\delta)^2}.$$

As ν_1 and ν_2 are experimentally determined and l_1 and l_2 are read off the bar, we can determine δ from the quadratic equation above formed. The positive value of δ is then taken as the end-correction.

Experimental.

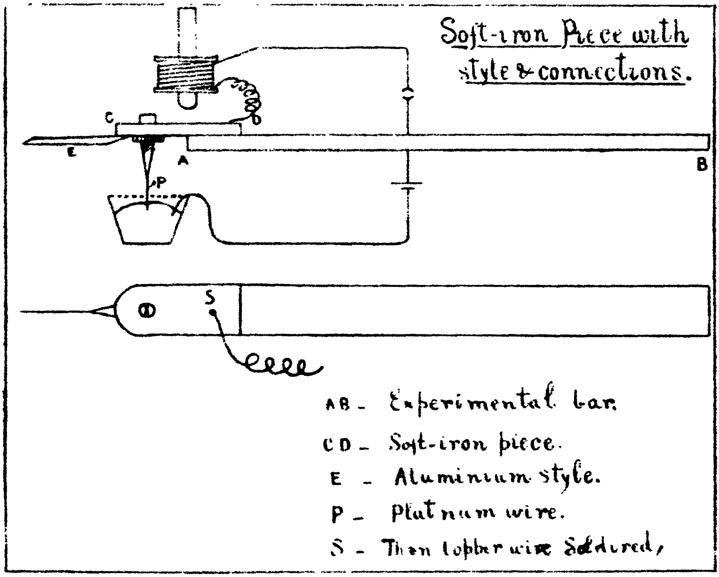
The important quantity to be determined in the formula is the frequency of the vibrating bar. For this purpose a smoked cylinder rotating at a known speed was used, and an aluminium style fixed to the free end of the bar kept vibrating electrically was allowed to record its vibrations on the drum. For each length of the bar at least two separate records were obtained from which the mean frequency was calculated.

It might be worth while recording here that for the electrical maintenance of the vibrations it was necessary to fasten a small thin sheet of soft iron by means of a little sealing-wax at the free end of the bar when non-magnetic materials were used for experiment. With the aid of this device it was possible to work with all kinds of materials. The design of the style with the soft iron piece is shown in fig. 1. The vibrating bars were clamped firmly in a vice fixed to a strong table at any desired cm. mark made on them.

A Specimen Calculation and Procedure.

A curve is drawn between readings of the cm. divisions at which the bar is successively clamped, and the corresponding frequencies determined from the smoked drum.

Fig. 1.



From the curve so drawn, frequencies at some points of the clamp other than those actually used in the experiment are also read.

The length between the cm. mark at which the bar is clamped and some convenient division near the free end beyond which the soft iron piece is fixed is noted for each position of clamp of the bar. The end-correction then applies to this division taken as the zero. Thus, if beginning from the free-end as 0 cm. mark, the bar is clamped at 21 cm. mark and the iron piece extends up to, say, near 3 cm. mark, the length between the 21st cm. mark and the 4th cm. mark is taken, that is, $l = (21 - 4) = 17$ cm. The corrected length, then, is $(17+\delta)$. For other points of clamp the same procedure is followed.

For accurately determining δ_1, four values of l and the corresponding ν are chosen well distributed over the l–ν curve. Two equations are then formed and δ determined from each independently. The mean of the two is then taken to be the end-correction.

As an example we will take the case of brass :—

Mean thickness of brass bar (with screw-gauge).........................	0·1527 cm.
Density of the brass	8·48 gr./cm.^{3}

The two equations for determining δ are :

$$\frac{70\cdot50}{25\cdot87}=\frac{(11+\delta)^2}{(4+\delta)^2}\ldots\text{(i.)}\quad\text{and}\quad\frac{49\cdot50}{18\cdot75}=\frac{(14+\delta)^2}{(6+\delta)^2}\ldots\text{(ii.)}.$$

From (i.) we get

$$\delta^2-0\cdot14\delta-45\cdot04=0,$$

or $$\delta=+6\cdot78 \text{ or } -6\cdot64.$$

From (ii.), similarly, we have

$$\delta^2+2\cdot24\delta-61\cdot56=0,$$

or $$\delta=+6\cdot80 \text{ or } -9\cdot04.$$

Thus mean $\delta = 6\cdot79$ cm.

Table I. gives the results of observations :—

TABLE I.

Obs.	ν.	$\nu^2=y$.	l, in cm.	$L=(l+\delta)$, in cm.	$\frac{1}{L^4}=x$.
1.........	15·90	252·81	17·0	23·79	$3\cdot12\times10^{-6}$
2.........	18·75	351·56	14·0	20·79	5·35 „
3.........	25·87	669·26	11·0	17·79	9·98 „
4.........	37·25	1387·56	8·0	14·79	20·89 „
5.........	49·50	2450·25	6·0	12·79	37·37 „
6.........	70·50	4970·25	4·0	10·79	73·77 „
7.........	85·15	7250·52	3·0	9·79	108·86 „

The result is shown graphically in fig. 2, from which

$$\text{Mean } \tan\theta = 6{\cdot}67 \times 10^7.$$

Thus
$$A = \tan\theta = \frac{q \,.\, t^2 \,.\, m^4}{\rho \,.\, 48\pi^2} = 6{\cdot}67 \times 10^7,$$

or
$$\frac{q}{\rho} = \frac{6{\cdot}67 \times 10^7 \times 48\pi^2}{(0{\cdot}1527)^2 \times (1{\cdot}8751)^4}$$
$$= 1{\cdot}096 \times 10^{11},$$

or
$$q = 1{\cdot}096 \times 8{\cdot}48 \times 10^{11} \text{ dynes/cm.}^2$$
$$= 9{\cdot}29 \times 10^{11} \text{ dynes/cm.}^2$$

The results obtained with a few other materials by the method outlined in this paper are given in Table II. For the sake of comparison, the Young's moduli of the very same bars were also determined by the ordinary flexure method and are included in the table.

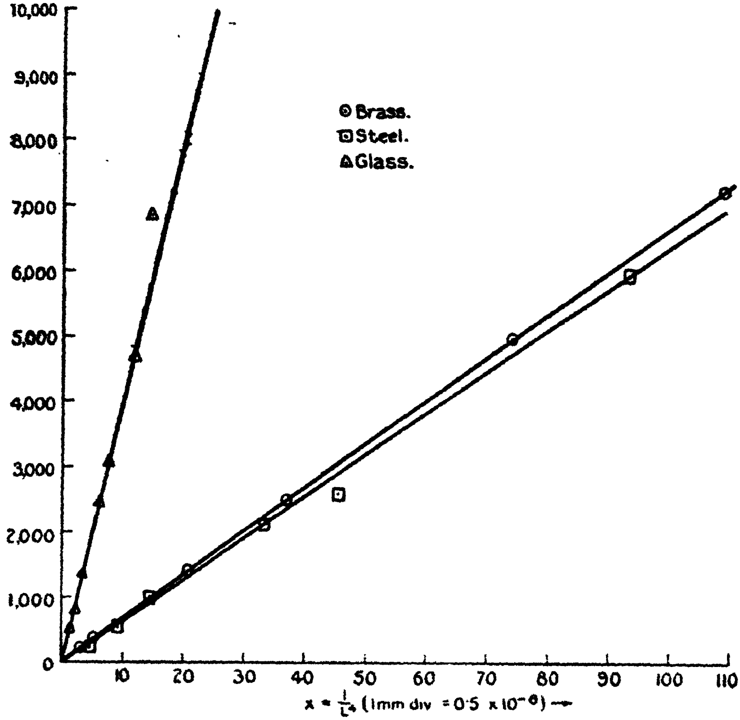
TABLE II.

No.	Material.	Density.	q—by Author's method, in dynes/cm.^{2}	q—by flexure method, in dynes/cm.^{2}	q—from Kaye & Laby's table of constants, in dynes/cm.^{2}
1......	Steel.	7·80	$19{\cdot}49 \times 10^{11}$	$20{\cdot}26 \times 10^{11}$	$19{\cdot}5$–$20{\cdot}6 \times 10^{11}$
2......	Brass.	8·48	9·29 ,,	9·79 ,,	9·7–10·2 ,,
3......	Glass.	2·54	7·56 ,,	6·38 ,,	6·5– 7·8 ,,
4......	Ebonite.	1·255	0·091 ,,	0·24 ,,	×

It would be noticed by reference to fig. 2 for ebonite that it is not straight over the whole course and does not pass through the origin. The explanation of this is that the soft iron piece was too heavy for the ebonite strip used, and that during the oscillations the ebonite got strained beyond the elastic limit. Over the portion of the curve convex to the axis of $\frac{1}{L_4}$, the value of $\tan\theta$ continuously decreases, giving smaller and smaller values to q.

In conclusion, I have to thank Mr. K. Dayal, M.Sc., of the Physics Department, for kindly determining the values of q for the materials by the flexure method. I have also to thank Mr. R. P. Gupta, M.Sc., for help in determining the frequencies of the vibrating bars.

Fig. 2.



[*Added in proof.*—It has not been possible to show the graph conveniently for ebonite in fig. 2 on the scales adopted for the other materials.—K. P.]

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LXIV. *The Energies of Dissociation of Cadmium and Zinc Molecules from an Interpretation of their Band Spectra.* *By* J. G. Winans, *Ph.D., National Research Fellow*[*]

[Plate XIV. figs. 1 & 2.]

Introduction.

THE absorption spectrum of cadmium at pressures below 1400 mm. has been studied by Mohler and Moore(1). They have observed a group of bands near 3261, a continuous band extending from below 2288 to longer wavelengths and terminating in a series of flutings between $\lambda\lambda$ 2781 and 2653, and a band at 2212. Jablonski(2) observed a continuous band from 2112–2135 with a maximum of intensity at 2114. Further observations of these bands described below show very interesting changes with pressure which can be interpreted on the basis of a set of molecular energy levels.

Apparatus.

The absorption cells, one 32 cm. and one 18·7 cm. long, were made of fused quartz with flat end-plates. Cadmium or zinc was distilled into the cell after evacuation and baking, and the cell was sealed off at a temperature near 600° C. It was then supported in a furnace arranged to prevent condensation of metal on the windows. A hydrogen discharge-tube similar to one described by Lambrey and Chalonge(3) served as a good source of continuous light. Spectra were photographed with sizes E 2 and E 31 Hilger quartz spectrographs.

Absorption Spectrum of Cadmium.

The development of the band absorption in cadmium vapour as the pressure is increased is shown on Pl. XIV. (fig. 1, #1–16). At low pressures the 2288 (1^1S-2^1P) cadmium resonance line appears as a narrow absorption line, and then broadens symmetrically with pressure until it is over 60 Å. wide. It overlaps the 2212 band at pressures greater than 60 mm., but does not broaden beyond this band at 186 mm., although the long-wave limit extends as far as 2530 Å. At pressures over 130 mm. a set of broad and diffuse flutings are seen on the long wave-length side of this band. These flutings extend from λλ 2650 to 2780 and converge toward the violet. Their wave-lengths and frequencies are given by Mohler and Moore (1). The bands at 2212 and 2114 appear at 7 mm. The 2212 band broadens a little toward longer wave-lengths, and the 2114 band broadens slightly in both directions with increasing pressure.

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[*] Communicated by the Author.

THE SPECTRUM OF THE ELECTRODELESS DISCHARGE IN CADMIUM.

Cadmium contained in a sealed quartz tube was heated by a Bunsen flame, and a discharge was produced in the tube through a single external electrode attached to a low-voltage Tesla coil.

In fig. 1 (Pl. XIV., ♯17) is seen the spectrum of this discharge. It showed principally the lines of the cadmium arc spectrum, but the higher series lines near the convergent limit of the triplet S and D series were more strongly developed than in the spectrum of the cadmium arc. The band at 2114 appears strongly, but the 2212 band *failed to appear*. These two bands at 2212 and 2114 have nearly equal intensities in absorption, but only the 2114 band appears in the electrodeless discharge. This is seen on comparing ♯17 with ♯1–16 in fig. 1 (Pl. XIV.).

A continuous spectrum extends from 4800 to 2240 with maxima of intensity at 4400, 3300, 2980, and 2288. There is a decrease in intensity at 3260, a faint maximum at 2980, then a gradual increase in intensity to 2288, and rapid decrease to zero at wave-lengths less than 2288. The last observable trace is at 2220.

Two spark resonance lines, 2133·4 and 2265·0, and faint traces of a few other spark lines were observed in the spectrum of the electrodeless discharge.

THE ABSORPTION SPECTRUM OF ZINC.

The absorption spectrum of zinc is similar to that of cadmium. At pressures over 730 mm., Mohler and Moore (1) observed a group of bands near 3000, a set of flutings from 2636–2551, and continuous absorption below 2550. With the arrangement of apparatus as previously described (4), other absorption bands at 2064 and 1997–2006 are observed. These bands are shown on Pl. XIV. (fig. 2, ♯1–3). The zinc absorption line at 2139 (1^1S-2^1P) broadens into a band with increasing pressure, exactly as the cadmium resonance line 2288 shown on Pl. XIV. (fig. 1, ♯1–16).

The short-wave limit of the zinc band comes at 2064. The flutings observed by Mohler and Moore were not found in this work—probably due to insufficient vapour-pressure.

DISCUSSION.

The Band Spectrum of Cadmium.—The observations on the cadmium band spectrum can be briefly stated as follows. The absorption line 2288 broadens into a band with increasing pressure. It reaches a definite limit at 2207 on the violet side, and on the red side extends to 2800, terminating in a series of flutings. These flutings converge towards the violet. Two absorption bands appear at 2212 and 2114, but only the 2114 band is observed in emission in the electrodeless discharge. In the electrodeless discharge the cadmium line 2288 is surrounded by a continuous spectrum which decreases in intensity rapidly at wave-lengths below 2288, and gradually for wave-lengths above 2288.

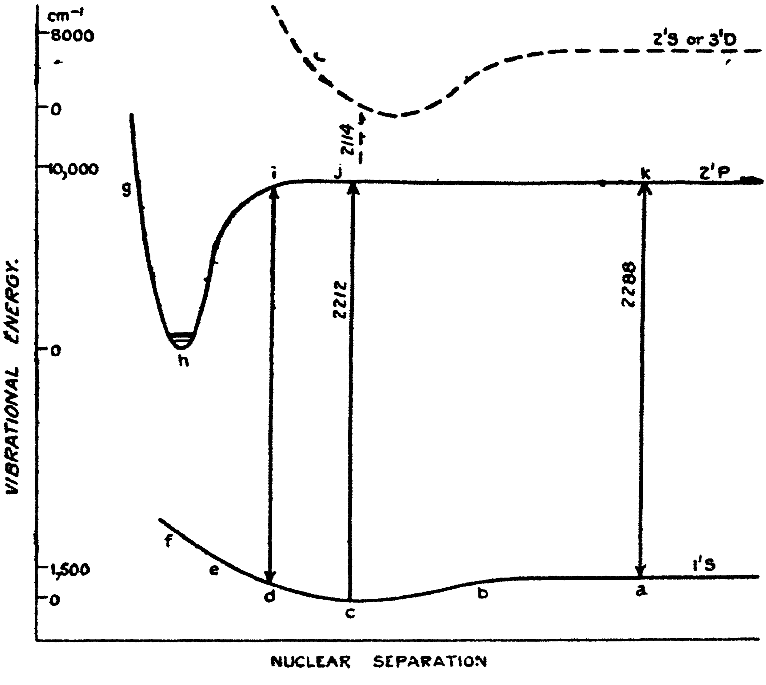
It is natural to seek for an interpretation of these observations in terms of absorption and emission by cadmium molecules. A clear way to picture the absorption and emission processes in a molecule is to draw the curves of vibrational energy as nuclear separation for the different electronic states of the molecule. By a series of arguments, which will be presented below, one can show that two of the electronic states in the cadmium molecule are probably represented by an arrangement of curves like those shown in fig. 4.

Granting for the moment that the relative shapes and positions of the curves are correct, we can see how the experimental observations can be explained. According to a principle first given by Franck(5) and extended by Condon(6), only those transitions will occur for which the position and momentum of the nucleii in the initial state equal the position and momentum in the final state. Further, since a vibrating dipole spends most of its time near the ends of its vibrations, transitions are most likely to occur when the nuclei are at either their maximum or minimum displacements. This means that in fig. 4 the most probable transitions are represented by vertical lines from the ends of the vibration levels on one potential energy curve to the ends of the vibration levels in the curve for another electronic state.

In fig. 4, the 2212 band is represented by an absorption *cj* from the non-vibrating state of the normal molecule to the flat part of the potential energy curve of the excited state.

This means that after absorption of 2212 by a Cd$_2$ molecule the two cadmium atoms will be free to drift apart, one of them being in the 2^1P atomic state. As soon as the pressure is high enough for the formation of a sufficient number of molecules to show absorption, the 2212 band should appear, and with increasing pressure and temperature should broaden only towards the red. It represents the shortest wave-length absorption possible with the curves as shown in fig. 4. This agrees with the development of the 2212 band with pressure

Fig. 4.



Potential-energy curves for the cadmium molecule.

as shown in Pl. XIV. (fig. 1, ♯1–16). There is no atomic line of cadmium at 2212. This band must be attributed to molecular absorption. Also, this band being represented by an absorption from a stable molecular state into an unstable one should appear in absorption but *not in emission*, and this is exactly that which was observed. Compare numbers 17 and 1–16 in fig. 1 (Pl. XIV.).

The broadening of the 2288 line into a band, with pressure, is represented by absorptions from quasi-molecules, as discussed by Born and Franck(7). When two atoms collide, their mutual potential energy follows the potential energy curve for the molecule. If either atom absorbs light during collision, the wave-length absorbed will be determined by the molecular energy-level curves. Two slowly-moving atoms in collision, following the curve *abcdef* in fig. 4, have their maximum velocity at *c* on approach and departure, and come instantaneously to rest near *d*. The probability of absorption of light is greatest near *d* and *b*, and least near *c*, due to the relative amount of time spent at these places during a collision. Absorption from the region *de* gives a wave-length longer than the atomic line, and absorption from *dc* and *cb* gives a wave-length shorter than the atomic line. With increasing pressure and energy of the colliding atoms, the absorption will extend to longer wave-lengths corresponding to absorption from the region *def*, and to shorter wave-lengths as far as the limit set by the 2212 band (absorption *cj*). The 2288 cadmium line should then broaden with pressure into a band, limited on the short-wave side by the 2212 band, but not so limited on the long-wave side. This asymmetrical broadening is exactly that shown in fig. 1, ♯1–16 (Pl. XIV.).

The electrodeless discharge shows the 2288 line in emission surrounded by a continuous spectrum. This is represented in fig. 4 by the excitation of quasi-molecules from the region *cde* through electron impacts. A stable excited molecule is formed which later emits a continuous radiation corresponding to the energy received. The probability of excitation is again greatest at *d*, and the energy received corresponds to wave-lengths near 2288. The main features of the absorption band should then appear in the emission band, but without the emission of the 2212 band, since the initial state for this band is unstable. The continuous spectrum surrounding 2288, shown in fig. 1, ♯17 (Pl. XIV.), has the features expected from fig. 4, and the 2212 band failed to appear as also expected from fig. 4. The faint maximum at 2980 may be due to emission by excited molecules which have lost their vibrational energy through collisions of the second kind.

So far we see that the observations shown in fig. 1 (Pl. XIV.) on the absorption bands 2212 and 2207–3000 in cadmium can be explained by a set of potential-energy curves as shown in fig. 4. Also, these curves explain the continuous spectrum surrounding the 2288 line and the non-appearance of the 2212 band in the electrodeless discharge.

This success in explaining observations is evidence that the curves in general characteristics are correct, but one naturally wishes also for a more general justification on the basis of band-spectrum constants. The band-spectrum constants are not known; but from analogy with other molecules it can be shown that these curves are to be expected for the cadmium molecule.

Zinc, cadmium, and mercury vapours are non-atomic at low pressures; at pressures over 10 mm., molecules are formed which give rise to band absorption. By measuring the decrease in intensity with superheating of the mercury band at 2540, Franck and Grotrian (8) and Koernicke (9) computed the energy of dissociation of Hg_2 to be about 0·06 volt. An energy of dissociation of this order of magnitude is to be expected for cadmium and zinc. If Cd_2 has a low heat of dissociation, it is seen through an empirical relation of Bates and Andrews (10),

$$\left.\begin{array}{l}\dfrac{D}{(\omega^0)^2\mu} = \text{a constant for all homopolar molecules to} \\ \qquad\qquad \text{within 30 per cent.,} \\ D = \text{energy of dissociation,}\end{array}\right\} \quad (1)$$

that $\omega^{0''}$ is small. A small value of $\omega^{0''}$ means a wide shallow potential-energy curve for the normal state. The potential-energy equation is (11)

$$\left.\begin{array}{l}v = u_2(r-r_0)^2 + u_3(r-r_0)^3 + \ldots, \\ u_2 = [0\cdot95641-3]\,[(\omega^0)^2\mu].\end{array}\right\} \quad . \quad . \quad . \quad (2)$$

The quantity in brackets is the logarithm of the coefficient. v and ω^0 are in cm^{-1}, $r-r_0$ in Ångström units,

$$\frac{1\cdot65}{\mu} = \frac{1}{M_1} + \frac{1}{M_2},$$

where M_1 and M_2 are the atomic weights of the atoms. The parabolic approximation to equation (2) given by the first term can be obtained when only ω^0 is known.

The continuous band surrounding 2288 extends over a range corresponding to an energy greater than that which we should expect for the energy of dissociation of the normal molecule. It is then necessary to attribute this wide extent to the range of vibration levels in the excited state, and say that the energy of binding of the excited molecules is greater than that of the normal molecules. This is almost certain for such molecules as Zn_2, Cd_2, and Hg_2, and means in general, though not always, that $\omega^{0'} > \omega^{0''}$ (from 1), the potential energy curve for the excited state, is narrower than that for the normal state (from 2), and the minima come at $r_0' < r_0''$. This last comes from another empirical rule,

$$\left.\begin{aligned} \omega^{0''}I_0'' &= \omega^{0'}I_0' \\ \text{or} \qquad \omega^{0''}r_0''^2 &= \omega^{0'}r_0'^2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to within 20 per cent. for the different states in one molecule.

When the atoms of a molecule are separated, the curves of potential energy against nuclear separation become the energy levels of the atoms. The limit of the curve *abcdef* for the normal cadmium molecule is the normal state of the cadmium atom 1^1S. The limit of the curve *ghijk* for the excited state is taken as the 2^1P cadmium atomic state. This is indicated by the development of the absorption band out of the line 1^1S-2^1P λ 2288, as shown in fig. 1, ♯ 1–16 (Pl. XIV.). Also, the 1^1S-2^1P is the only cadmium atomic transition in the region of the band from 2207–2800.

In this way, from the assumption of a low heat of dissociation for Cd_2 in analogy with mercury, and associating the width of the band from 2207–2800 with the range of vibration states in the excited molecule, we are led to a probable picture of the energy levels of Cd_2 as shown in fig. 4. These levels are in themselves consistent, and explain the experimental facts as described above. The relative positions shown in fig. 4 are the only positions which will explain the observations.

In fig. 4 the energy of dissociation of Cd_2 is given by the difference in energy between points *a* and *b* on curve *abcdef*, and this difference is given by the difference in energy between the 2288 line and the short-wave limit of the 2212 band. This energy difference is 1600 cm.$^{-1}$, 0·200 volt, or 4·7 kg. cal.

The Band Spectrum of Zinc.—The general features of the zinc absorption bands, shown in fig. 2, ♯ 1–3 (Pl. XIV.), are the same as those for the cadmium bands. Assuming the same kind of curves as those of fig. 4, the energy of dissociation of Zn_2 is 2000 cm.$^{-1}$, 0·246 volt, or 5·7 kg. cal.

Energies of Dissociation of Zn_2, Cd_2, and Hg_2.—It is interesting to compare the energies of dissociation of zinc, cadmium, and mercury molecules, as obtained here and by Koernicke, with the heats of fusion. The energy absorbed in melting a metal into freely-moving atoms might be expected to be proportional to the energies of dissociation of the molecules. This is found to be true for zinc, cadmium, and mercury, as shown in Table I.

Absorption Coefficients for Singlet and Triplet Systems.—One might wonder why no band appears near the cadmium line 3261 ($1^1S-2^3P_1$) due to molecular states which converge toward the three triplet P-levels. By comparison of the pressures at which 2288 (1^1S-2^1P) and 3261 (1^1S-2^1P) first appear in absorption, one can estimate the relative absorption coefficients of cadmium vapour for these lines. In this way it is found that the coefficient for 2288 is 7000 times that for 3261. In fig. 1, #16 (Pl. XIV.) the band absorption in the region of 2288 is fully developed, while the 3261 line has just appeared as a narrow line, and there is no sign of bands in the region of 3261. Since the transitions between levels of the singlet system are so much more probable than those between singlet and triplet systems, we need to consider only the singlet terms in our discussion of the absorption bands near 2288 shown in fig. 1 (Pl. XIV.).

TABLE I.

Comparison of Heats of Fusion and Energies of Dissociation.

Metal.	H, cal./grm.	Atomic weight.	H, cal./mole.	$H\times\frac{4}{3}\times10^{-4}$.	D, volts.
Zn ……	28	65	1800	0·24	0·25
Cd ……	13·7	112	1500	0·20	0·20
Hg ……	2·8	200	560	0·07	0·06

The Cadmium Band at 2114.—This band was observed by Jablonski⁽²⁾, who found it in absorption and in fluorescence. It was also observed in the electrodeless discharge by Kapuscinski, and by de Groot in the positive column discharge through a mixture of cadmium and argon. It was observed in this work in absorption, and in emission in the electrodeless discharge. Jablonski⁽²⁾ also found that absorption by cadmium vapour of light in the region of this band resulted in the emission of the triplet $2^3P_{2,1,0}-2^3S$ in fluorescence.

This band, which is observed both in emission and absorption, should be represented by a transition between stable molecular states. Its appearance in absorption at about the same pressure as 2212 (see fig. 1, #1–16 (Pl. XIV.)) indicates that it is also due to an absorption by normal Cd_2 molecules. Since the singlet-triplet absorptions are very much less probable than the singlet-singlet absorptions, it is natural to associate the 2114 band with a transition from the normal molecule to a molecular state whose vibration levels converge to some singlet atomic level above 2^1P. The next singlet atomic levels are 2^1S and 3^1D.

Representing a molecular state by the dotted curve shown in fig. 4, one can explain the broadening of the 2114 band with pressure, the difference of wave-length of the maximum in absorption and emission observed by Jablonski(2), the fluorescence observations of Jablonski[2], and the appearance of this band in absorption at nearly the same pressure as 2212. The sharp triplet in fluorescence is assumed to result from collisions of the second kind between excited cadmium molecules and normal cadmium atoms.

This hypothesis for the cadmium band 2114 applies also to the corresponding zinc absorption band at 2002 shown in fig. 2 (Pl. XIV.).

Flutings in the Band Spectrum of Cadmium.—Mohler and Moore(1) observed a series of flutings between 2781 and 2653 in absorption, and Kapuscinski and Van der Lingen found a similar set of flutings between 3000 and 2650 in fluorescence in cadmium vapour. Kapuscinski also found that cadmium vapour re-emitted in fluorescence several lines of wave-length within the limits of the fluorescence band 3000-2288. Walter and Barratt have recently stated that these flutings may be due to impurities such as CdO. If this is true, it must be assumed that in the region between 2800 and 2300 the bands of the impurities are so closely spaced that practically any frequency in this region can be absorbed and later emitted, in accordance with the observations of Kapuscinski.

These observations, however, can be explained on the basis of fig. 4, and the flutings attributed to Cd_2 molecules. Two colliding cadmium atoms which absorb energy and form a stable excited molecule will from the Franck-Condon principle, favour those transitions which can be represented by vertical lines from the region *def* to the ends of the vibration levels in the excited state. When one curve is much steeper than the other, as those in fig. 2, this may result in rises and falls of intensity in the continuous absorption region. This would appear as a series of flutings on the long wave-length edge of the absorption band which grows out of 2288. Two colliding atoms which absorb light in the region 2800–3000 will form an excited molecule which can later emit the energy received as a fluting of the same wave-length. This is a possible explanation of the observations.

SUMMARY.

1. New observations on the absorption spectrum in cadmium vapour show the development of the atomic line 2288 into a band from 2207–2800 with increasing pressure. The absorption bands at 2212 and 2114 were also observed.

2. The electrodeless discharge in cadmium vapour shows a continuous spectrum with maxima at 2288, 2980, 3000, and 4400. The band at 2114 appears, but the 2212 band is noticeably absent.

3. The cadmium band from 2207 to 2800 is attributed to absorption of light by two colliding atoms, the end product being a stable excited molecule. This view explains the development of the absorption band with pressure, the appearance of the 2212 band in absorption but not in emission, the continuous spectrum in the electrodeless discharge between 2220 and 3000, and yields a value of 0·200 volt for the energy of dissociation of Cd_2.

4. Applying the same explanation to the absorption spectrum of zinc gives an energy of dissociation of 0·246 volt for Zn_2.

5. The energies of dissociation of zinc, cadmium, and mercury molecules are found to be proportional to the atomic heats of fusion.

6. The 2114 band of cadmium and the corresponding band at 2002 in zinc can be represented by an absorption to a stable molecular state whose vibration levels converge to 2^1S or 3^1D.

7. A possible explanation is given for the flutings between 3000 and 2650 observed in absorption and fluorescence.

In conclusion, I wish to express my thanks to Professor K. T. Compton for the privilege of working in the Palmer Laboratory, and to Professors E. U. Condon and F. W. Loomis for helpful discussions on the subject of this paper.

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(1) F. L. Mohler and H. R. Moore, J. O. S. A. xv. p. 74 (1927).
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(6) E. U. Condon, Phys. Rev. xxviii. p. 1182 (1926).
(7) M. Born and J. Franck, *Zeit. f. Phys.* xxxi. p. 416 (1925).
(8) Franck and Grotrian, *Zeit. f. Tech. Phys.* iii. p. 194 (1922).
(9) Koernicke, *Zeit. f. Phys.* xxxiii. p. 219 (1925).

(10) J. R. Bates and D. H. Andrews, Proc. Nat. Acad. Sci. xiv. p. 124 (1928). The form given here is obtained by eliminating the K between the two equations given by Bates and Andrews. When D is in volts, ω^0 in cm.$^{-1}$, and μ in units of 10^{-24} grm., the value of the constant is $2{\cdot}9\times10^{-7}$.

(11) E. U. Condon, *loc. cit.* p. 1194.

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LXV. *Flutings in the Absorption Spectrum of a Mixture of Mercury and Cadmium Vapours. By* J. G. WINANS, *Ph.D., National Research Fellow* *.

[Plate XIV. fig. 3.]

DURING the experiments described in the preceding paper, one absorption cell was prepared with a mixture of cadmium and mercury.

In the absorption spectrum of this mixture of cadmium and mercury the 2288 line of cadmium appears and broadens with pressure into a band in the same way as in pure cadmium, and a new set of flutings is observed on the long wave-length edge of the band. They are shown on Pl. XIV. (fig. 3, ♯3 and 4). These flutings are diffuse, like those in pure cadmium, and are difficult to measure accurately. Their wave-lengths and frequencies are given in Table I. Wave-lengths were measured at intensity maxima.

The partial pressures of mercury and cadmium at which these flutings appear may be obtained approximately by comparing the widths of the mercury and cadmium bands in the mixture with a series of absorption spectra of pure mercury and cadmium taken at different pressures. In this way it is found that the cell contained mercury at 100 mm. and cadmium at 60 mm. pressure.

These flutings are similar in character to flutings observed in mercury, cadmium, and zinc by Rayleigh ⁽¹⁾ and Mohler and Moore ⁽²⁾. Walter and Barrett ⁽³⁾ have recently mentioned having evidence that some of these flutings are due to impurities. This may also be true of these flutings in the mixture of mercury and cadmium, although they were not observed in mercury alone, or cadmium alone, at pressures up to 180 mm. If they were due to Hg_2, Cd_2, or

* Communicated by the Author.

TABLE I.

Flutings in the Absorption Spectrum of a Mixture of Cadmium and Mercury.

Wave-length.	Wave-number.	Δν.
2488·6	40171	
		140
2480·0	40310	
		122
2472·5	40433	
		112
2465·6	40545	
		103
2459·4	40648	
		96
2453·6	40744	
		85
2448·5	40829	
		82
2443·6	40911	
		80
2438·8	40991	
		79
2434·1	41070	
		69
2430·0	41139	
		67
2426·1	41206	
		66
2422·3	41270	
		61
2418·7	41331	
		77
2414·2	41408	
		57
2410·9	41465	
		69
2406·8	41536	

an impurity in either, they would be expected to appear in mercury or cadmium alone. They are therefore most likely due to HgCd molecules.

References.

(1) Rayleigh, Proc. Roy. Soc. Lond. cxiv. p. 620 (1927); cxvi. p. 702 (1927).
(2) F. L. Mohler and H. R. Moore, J. O. S. A. xv. p. 74 (1927).
(3) J. M. Walter and S. Barratt, 'Nature,' cxxii. p. 684 (Nov. 3, 1928), p. 748 (Nov. 10, 1928).

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August 30, 1928.

LXVI. *The Measurement of Conductivities by means of Oscillating Circuits. By* S. D. Gehman *and* B. B. Weatherby, *University of Pennsylvania*[*].

IN a recent issue of the Philosophical Magazine[†], Burton and Pitt report on certain experiments in which they claim to have measured the conductivities of various solutions and organic liquids. The paper is entitled "A New Method of Conductivity Measurement by means of an Oscillating Valve Circuit."

We wish to point out that the changes in distributed capacity caused by inserting the glass tube containing the liquids worked with into the coils of the oscillating system described by Burton and Pitt are sufficient to produce serious frequency changes in the circuit—changes which would affect the interpretation of the results recorded. It is surprising that the losses on which the authors must be depending to furnish an indication of the conductivity do not continue to increase the effects as the conductivities of the solutions are increased. The changes in instrumental deflexion with change in concentration of the KCl solutions are certainly not what one would expect on the assumption that the relation between the conductivity and concentration within the limits used is a linear one.

It is our opinion that the effects reported by Burton and Pitt are to be ascribed to the dielectric constants of the liquid used. We tabulate below the deflexions they publish for organic liquids, and in a parallel column the accepted values for the dielectric constants of these liquids.

Liquid.	Deflexion.	Dielectric constant.
Hexane	6·8	1·9
Pentane	8·8	1·8
Xylene	15·3	2·5
Xylol	11·8	
Toluene	14·0	2·3
Toluol	15·1	
Carbon tetrachloride	17·2	2·2
Benzol	18·0	2·3
Amyl alcohol	23·7	16·0
Ether	32·3	4·3
Chloroform	42·5	5·2
Butyl alcohol	71·4	19·2
Ethyl alcohol	77·2	25·8

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[*] Communicated by Prof. C. B. Bazzoni, Ph.D.

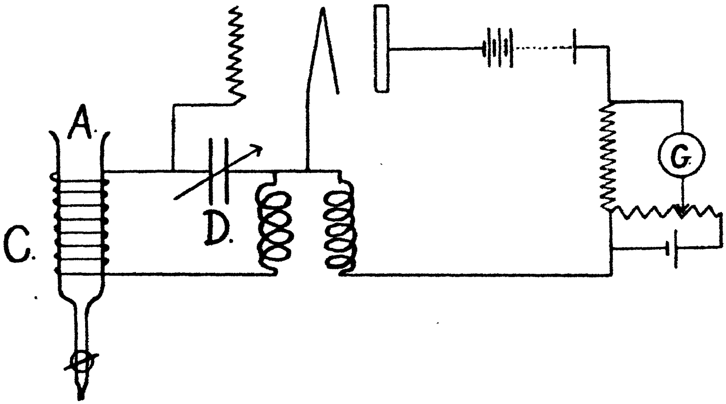
[†] Phil. Mag. v. p. 939 (1928).

The only marked exception to the ranking of deflexions in the order of the dielectric constants is in the case of amyl alcohol.

In order to check this idea we built up a circuit duplicating that of Burton and Pitt in all essential features, and observed the deflexions obtained with acetone and glycerine. These were selected because their conductivities as compared by us in a usual manner were in the reverse order of their dielectric constants. It is to be observed that the deflexions are in the order of the dielectric constants and not in the order of the conductivities.

Liquid.	Comparative conductivity.	Dielectric constant.	Deflexion.
Acetone	5·6	21·5	44 cm.
Glycerine	1·0	56·2	66 „

We pushed the matter a little further, using the circuit shown in the figure.



The oscillation frequency was about 600,000 cycles per second. The circuit was quite sensitive enough for the purpose at hand. The liquids were introduced into the glass vessel A, around which was wrapped a coil, C.

By using this arrangement any effects due to an alteration of the coupling between the plate and grid circuits and any losses in the plate circuit due to the introduction of the liquid were eliminated. This was found advisable because in the Burton and Pitt apparatus the deflexion depended upon how far the liquid was lowered into the plate coil.

The deflexions obtained with this arrangement duplicated satisfactorily those which we secured with the more complicated circuit used by Burton and Pitt.

With this apparatus, deflexions were secured for solutions of KCl of various concentrations, and a curve was plotted. A condenser with paraffined plates was then shunted across D. This condenser was filled successively with the same solutions that had been used in the coil. The deflexions obtained were identical in nature with those secured when the coil was used.

We consequently feel safe in ascribing the effects obtained by Burton and Pitt primarily to the dielectric constants of the liquids used.

LXVII. *The Motion of a Particle on a Rough Sphere, including the Case of a Rotating Sphere. By* A. F. STEVENSON [*].

IN this paper we investigate the motion of a heavy particle on the interior of a rough sphere, which may be either fixed or may rotate with constant angular velocity about a vertical diameter. The case where the sphere is smooth—the spherical pendulum—is of course well known, and, in this case, the motion of the particle in space is unaffected by the rotation of the sphere (even if the axis of rotation is not vertical and the angular velocity not constant). The case where there is friction, however, does not appear to have received much attention [†].

More positive conclusions can be drawn if a frictional force proportional to the velocity (or relative velocity) be assumed, rather than the more usual laws of friction, since the equations are thereby simplified and singularities avoided. This would correspond more nearly to the equivalent problem of the general motion of a single pendulum subject to air resistances, although, in this case, a resistance proportional to the square of the velocity would be nearer the truth. The case where the friction is of the usual type is also briefly considered.

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[*] Communicated by G. I. Taylor, F.R.S.

[†] It is only in a few simple types of surfaces, or in artificially-constructed cases, that the motion on a rough surface can be solved by quadratures. *Cf.* N. Basu, Phil. Mag. (6) p. 35 (1918).

Fixed Sphere.

1. Let a denote the radius of the sphere, θ the angle which the radius to the particle makes with the downward drawn vertical, ϕ the azimuth, and let the resistance to motion per unit mass be μ times the velocity. The equations of motion then are

$$\ddot{\theta}-\dot{\phi}^2\sin\theta\cos\theta=-\frac{g}{a}\sin\theta-\mu\dot{\theta}, \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{\sin\theta}\frac{d}{dt}(\dot{\phi}\sin^2\theta)=-\mu\dot{\phi}\sin\theta\,. \quad . \quad . \quad . \quad . \quad (2)$$

(2) may be written

$$\frac{dh}{dt}=-\mu h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $h=\dot{\phi}\sin^2\theta$. Multiplying (1) by $\dot{\theta}$, (2) by $\dot{\phi}\sin\theta$, and adding, we get

$$\frac{dE}{dt}=-\mu(\dot{\theta}^2+\dot{\phi}^2\sin^2\theta)=-2\mu\left(E+\frac{g}{a}\cos\theta\right), \quad . \quad (4)$$

where

$$E=\tfrac{1}{2}(\dot{\theta}^2+\dot{\phi}^2\sin^2\theta)-\frac{g}{a}\cos\theta.$$

(3) and (4) give the rates of dissipation of angular momentum and energy, respectively; we see that E and h continually decrease. Since the dissipative forces are proportional to the velocity, these equations could also be obtained by using Rayleigh's "dissipation function"[*].

2. From (3) we have

$$h=h_0e^{-\mu t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where h_0 is the initial angular momentum (we exclude the case $h_0=0$, which is that of the simple pendulum); hence the particle sinks asymptotically to the lowest position, as is evident *a priori*. To examine the motion more closely in the neighbourhood of $\theta=0$, substitute for $\dot{\phi}$ from (5) in (1), and retain only the lowest powers of θ. We thus obtain

$$\ddot{\theta}+\mu\dot{\theta}+\frac{g}{a}\theta=\frac{h_0^2e^{-2\mu t}}{\theta^3}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Putting $\theta=e^{-\mu t/2}\psi$, this becomes

$$\ddot{\psi}=\frac{h_0^2}{\psi^3}+\left(\frac{\mu^2}{4}-\frac{g}{a}\right)\psi.$$

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[*] Whittaker, 'Analytical Dynamics,' p. 230.

There are three types of solution for ψ:

(i.) If $\mu^2-4\frac{g}{a}>0(=\mu_1^2$, say), $\psi=A+Be^{\mu_1 t}+Ce^{-\mu_1 t}$.

(ii.) If $\mu^2-4\frac{g}{a}<0(=-\mu_2^2$, say), $\psi=A'+B'\sin(\mu_2 t+C')$

(iii.) If $\mu^2-4\frac{g}{a}=0$, $\psi=A''+(B''t+C'')^2$.

Here A, B, etc., denote certain constants depending on initial conditions. The general solution of (6) is thus obtained. We easily deduce that if $\mu^2\geq 4\frac{g}{a}$, then $\dot{\theta}$ vanishes at most once for finite values of t; but if $\mu^2<4\frac{g}{a}$, then $\dot{\theta}$ vanishes, in general, for an infinity of values of t, so that a rising and falling of the particle in the sphere persists (these results are analogous to those for the small damped oscillations of a simple pendulum). Thus in the former case the particle spirals into the bottom of the sphere, and there is no periodic motion; but in the latter (small friction) the motion is of a quasi-periodic type, similar to that of the ordinary spherical pendulum. In the latter case there is, in particular, no tendency for the path of the particle to become circular, as might perhaps be supposed at first; the limiting form of the motion is a small ellipse, as may be shown by taking Cartesian instead of polar coordinates, just as in the ordinary spherical pendulum*, the size of the ellipse decreasing asymptotically to zero.

Moreover, when θ is small, (5) gives

$$\dot{\phi}=\frac{h_0 e^{-\mu t}}{\theta^2}=\frac{h_0}{\psi^2},$$

from which the value of ϕ is easily obtained. We thus find that if $\mu^2\geq 4\frac{g}{a}$, $\dot{\phi}\rightarrow 0$ and ϕ tends to a finite value, as $t\rightarrow\infty$; but if $\mu^2<4\frac{g}{a}$, $\dot{\phi}$ does not, in general, tend to any definite limit, and $\phi\rightarrow\infty$.

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* Reference may be made to any text-book where the spherical pendulum is treated in detail, *e.g.*, Appell, 'Mécanique rationnelle,' vol. i. pp. 513 *et seq.*

3. So far no restriction has been placed on μ. If, however, we suppose μ small, then the particle may be considered to be moving approximately as in the ordinary spherical pendulum, and we can calculate the small corrections to be made. In this case, for values of t not too large, we may integrate (4) approximately in the form:

$$E = E_0(1-2\mu t)-\frac{2\mu g}{a}\int_0^t \cos\theta\, dt, \quad . \quad . \quad (7)$$

where E_0 is the value of E at $t=0$, and the integral on the right is calculated on the hypothesis of frictionless motion with the given initial conditions. In the spherical pendulum, $\cos\theta$ can be expressed as an elliptic function of the time in a form * which enables us to evaluate immediately the integral in terms of elliptic functions, if necessary.

Equations (7) and (5), which to the same order of approximation may be written

$$h = h_0(1-\mu t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

now constitute two first integrals of the equations.

Suppose that at $t=0$ the path of the particle is tangent to the circle $\theta=\alpha$, having there a velocity which, in the absence of friction, would make the path also tangent to $\theta=\beta\,(\beta<\alpha)$ —there is no loss of generality in this—and let the values of $\dot{\phi}$ at $\theta=\alpha, \beta$ be Ω_α, Ω_β respectively (these can, of course, be expressed in terms of α, β). Let us suppose that in the actual motion the next maximum of θ is given by $\theta=\alpha+\delta\alpha$. Then from (7), and using (8) to eliminate $\dot{\phi}$, we have for the value of E at $\theta=\alpha+\delta\alpha$

$$E_0(1-2\mu T)-\frac{2\mu g}{a}\int_0^T \cos\theta\, dt$$

$$=\frac{1}{2}\frac{h_0^2(1-u T)^2}{\sin^2(\alpha+\delta\alpha)}-\frac{g}{a}\cos(\alpha+\delta\alpha),$$

where

$$E_0=\frac{1}{2}\frac{h_0^2}{\sin^2\alpha}-\frac{g}{a}\cos\alpha\,;$$

$$h_0=\Omega_\alpha\sin^2\alpha\,;$$

and T denotes the "period"—*i. e.*, the time between successive minima for θ—in the frictionless case. Retaining only first powers of μ and $\delta\alpha$, we obtain

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* Whittaker, *l. c.* p. 105.

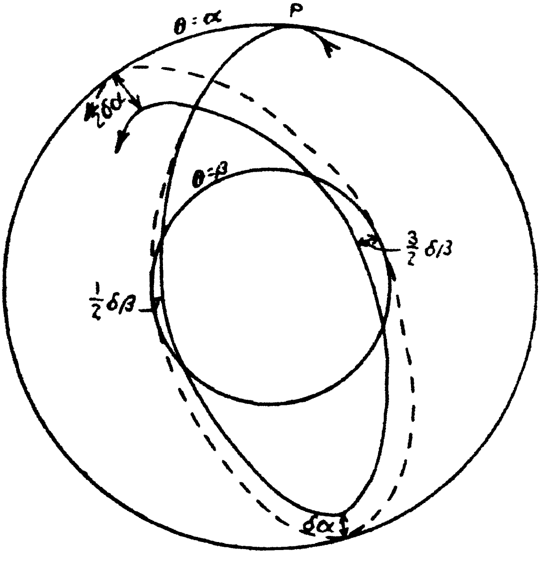
$$\delta\alpha = -\frac{2\mu(I-T\cos\alpha)}{\sin\alpha\left(1-\frac{a}{g}\Omega_\mu^2\cos\alpha\right)}, \quad . \quad . \quad . \quad (9)$$

where
$$I = \int_0^T \cos\theta\, dt.$$

Similarly, for $\delta\beta$, the increase in θ between successive minima for θ, we have

$$\delta\beta = -\frac{2\mu(T\cos\beta - I)}{\sin\beta\left(\frac{a}{g}\Omega_\beta^2\cos\beta-1\right)}, \quad . \quad . \quad . \quad (10)$$

Fig. 1.



the value of the integral being the same owing to symmetry in the frictionless case. Since both numerator and denominator are positive in the expressions on the right of (9) and (10), we see that $\delta\alpha$, $\delta\beta$ are both negative, as we would expect.

The increase in θ at the first minimum after projection is evidently $\frac{1}{2}\delta\beta$, to the same order, and that at the second minimum $\frac{3}{2}\delta\beta$. The character of the path of the particle, projected on a horizontal plane, is shown in fig. 1 (for the case where the motion is entirely in the lower hemisphere). The particle is supposed projected from the point P on the upper circle ($\theta=\alpha$), and the dotted curve represents the horizontal projection of the path in the frictionless case, the initial velocity being the same. The distances marked $\delta\alpha$, etc., correspond to the corrections given by (9) and (10). The actual horizontal distances are of course $a \cos\alpha\, \delta\alpha$, etc.

The integral I occurring in (9) and (10) may be expressed in terms of the period T by means of elliptic functions as in (7), or both I and T as elliptic integrals involving initial conditions. Thus we may consider the particle as moving between two horizontal circles on the sphere, these circles at the same time gradually sinking.

4. If $\alpha=\beta$, (9) and (10) fail, for then both numerator and denominator vanish. In this case we can use (1) directly. We now have

$$h_0^2=\frac{g\sin^4\alpha}{a\cos\alpha},$$

whence, substituting for $\dot{\phi}$ from (5) in (1),

$$\ddot{\theta}-\frac{g\sin^4\alpha\cos\theta}{a\cos\alpha\sin^3\theta}e^{-2\mu t}=-\frac{g}{a}\sin\theta-\mu\dot{\theta}.$$

For an interval of time not too large we can write $\theta=\alpha+\xi$, and retain only the first powers of ξ, $\dot{\xi}$, and μ. We thus obtain

$$\ddot{\xi}+\frac{g}{a}\xi\sec\alpha\,(\sin^2\alpha+4\cos^2\alpha)=-\frac{2\mu g}{a}t\sin\alpha,$$

whence the solution, with $\xi=\dot{\xi}=0$ when $t=0$,

$$\xi=\frac{\mu\sin 2\alpha}{\sin^2\alpha+4\cos^2\alpha}\left(\frac{1}{p}\sin pt-t\right),$$

where

$$p^2=\frac{g}{a}\sec\alpha\,(\sin^2\alpha+4\cos^2\alpha).$$

Thus, when next the path is horizontal ($\dot{\xi}=0$), θ has increased an amount

$$\delta_1\alpha=-\frac{2\pi}{p}\,\frac{\mu\sin 2\alpha}{\sin^2\alpha+4\cos^2\alpha}, \quad . \quad . \quad . \quad (11)$$

which corresponds to $\delta\alpha$ in the previous case. Thus the path of the particle is a downward spiral.

5. Consider now, briefly, the case where the friction is proportional to the normal reaction instead of to the velocity.

Eliminating the normal reaction from the equations of motion, we obtain as equations corresponding to (1) and (2)

$$\ddot{\theta}-\dot{\phi}^2\sin\theta\cos\theta=-\frac{g}{a}\sin\theta-\frac{\mu\dot{\theta}}{v}\left(v^2+\frac{g}{a}\cos\theta\right),$$

$$\frac{1}{\sin\theta}\frac{d}{dt}\left(\dot{\phi}\sin^2\theta\right)=-\frac{\mu\dot{\phi}\sin\theta}{v}\left(v^2+\frac{g}{a}\cos\theta\right),$$

where μ now denotes the (ordinary) coefficient of friction, and where $v^2=\dot{\theta}^2+\dot{\phi}^2\sin^2\theta$, the + sign being taken in front of the square root for v. The expression $v^2+\frac{g}{a}\cos\theta$ is proportional to the normal reaction inwards and is ordinarily positive; if, however, the conditions allow of it becoming negative, the sign must be changed when this occurs. These equations hold so long as $v\neq 0$, but if $v=0$ at any instant when $\theta=\theta_0$, then the particle will remain permanently at rest unless $\tan\theta_0>\mu$.

Using the same notation, (3) and (4) may now be written

$$\left.\begin{aligned}\frac{dh}{dt}&=-\mu h\frac{2\mathrm{E}+3\frac{g}{a}\cos\theta}{\sqrt{2\left(\mathrm{E}+\frac{g}{a}\cos\theta\right)}},\\ \frac{d\mathrm{E}}{dt}&=-\mu\left(2\mathrm{E}+3\frac{g}{a}\cos\theta\right)\sqrt{2\left(\mathrm{E}+\frac{g}{a}\cos\theta\right)}.\end{aligned}\right\}\quad(12)$$

Since the friction always opposes motion and does not now tend to zero with the velocity, it is evident that after a *finite* interval of time the particle will come to rest somewhere within the cone $\theta=\tan^{-1}\mu$, and not necessarily in the lowest position, as in the previous case.

If μ is small we can again integrate equations (12) approximately, the approximation holding for an interval of time not too large. The integrals can be briefly written

$$h=h_0\left(1-\mu\int_0^t\frac{\mathrm{R}}{v}dt\right);\qquad \mathrm{E}=\mathrm{E}_0-\mu\int_0^t\mathrm{R}v\,dt,$$

where Ra is the normal reaction per unit mass, and the integrals are calculated on the hypothesis of frictionless motion; they can be expressed as elliptic integrals.

By a precisely analogous method we now obtain in place of (9) and (10), and using the same notation,

$$\delta\alpha = \frac{-2\mu}{\sin\alpha\left(1-\frac{a}{g}\Omega_\alpha{}^2\cos\alpha\right)}\cdot\int_0^{\mathrm{T}}\frac{\mathrm{R}}{v}(\cos\theta-\cos\alpha)\,dt,$$

$$\delta\beta = \frac{-2\mu}{\sin\beta\left(\frac{a}{g}\Omega_\beta{}^2\cos\beta-1\right)}\cdot\int_0^{\mathrm{T}}\frac{\mathrm{R}}{v}(\cos\beta-\cos\theta)\,dt.$$

These differ from (9) and (10) only in the inclusion of the factor $\frac{\mathrm{R}}{v}$ in the two integrals, but μ has not, of course, the same significance. For the "conical pendulum" case we find corresponding to (11) by a similar method

$$\delta_1\alpha = -\frac{2\pi}{\mu}\,\frac{2\mu\sqrt{\frac{g}{a}\cos\alpha}}{\sin^2\alpha+4\cos^2\alpha}$$

Rotating Sphere.

1. Let ω denote the angular velocity of the sphere about the vertical diameter, and assume a resistance per unit mass equal to μ times the *relative* velocity. Then θ and ϕ denoting as before the coordinates of the particle *in space* (ω being measured in the same sense as ϕ), the equations of (absolute) motion are identical with (1) and (2) above, except that in the right-hand side of (2) we must replace $\dot{\phi}$ by $\dot{\phi}-\omega$. In place of (3) and (4) we then have

$$\left.\begin{aligned}\frac{dh}{dt} &= -\mu(h-\omega\sin^2\theta),\\ \frac{d\mathrm{E}}{dt} &= -\mu\left(2\mathrm{E}+\frac{2g}{a}\cos\theta-h\omega\right).\end{aligned}\right\}\quad . \quad . \quad (13)$$

We see at once that E and h do not now necessarily decrease; whether, at any time, they do so or not depends on the value of ω. Evidently the particle tends asymptotically to a position of relative rest, when θ and $\dot{\phi}\,(=\omega)$ will be constant. Now, it is easily seen from (1) that there are two possible positions of relative equilibrium given by $\theta=0$, or $\cos\theta=\frac{g}{a\omega^2}$, the second existing provided $\omega^2>\frac{g}{a}$. But from the appropriate condition for "permanent" stability, namely

$$\mathrm{V}-\mathrm{T}_0 = \text{minimum}\,^*,$$

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* Lamb, 'Hydrodynamics,' p. 291.

we see that the position $\theta=0$ is unstable if the second exists. Therefore the particle tends asymptotically to the bottom of the sphere or to a position of relative rest at

$$\theta = \cos^{-1}\frac{g}{a\omega^2},$$

according as ω^2 is less or greater than $\frac{g}{a}$*.

2. Although it does not appear possible to obtain any first integral of the equations, we can still regard the motion in space as being of the spherical pendulum type, the constants defining this motion slowly changing, provided μ is small and ω is not too large. We can then integrate equations (13) approximately for a limited period of time; the solutions involve the integrals $\int_0^t \cos\theta\,dt$ and $\int_0^t \sin^2\theta\,dt$, which can both be expressed explicitly in terms of t by means of elliptic functions. We thus find in place of (9) and (10)

$$\delta\alpha = \frac{-2\mu}{\sin\alpha\left(1-\frac{a}{g}\Omega_\alpha^2\cos\alpha\right)} \left[2(\mathrm{I}-\mathrm{T}\cos\alpha)-\frac{a}{g}\omega\Omega_\alpha(\mathrm{T}\sin^2\alpha-\mathrm{I}')\right],$$

$$\delta\beta = \frac{-2\mu}{\sin\beta\left(\frac{a}{g}\Omega_\beta^2\cos\beta-1\right)} \left[2(\mathrm{T}\cos\beta-\mathrm{I})-\frac{a}{g}\omega\Omega_\beta(\mathrm{I}'-\mathrm{T}\sin^2\beta)\right],$$

where the notation is the same as in (9) and (10), and where

$$\mathrm{I}' = \int_0^{\mathrm{T}} \sin^2\theta\,dt\,;$$

Ω_α, Ω_β refer to *absolute* values. I and I′ may both be expressed as elliptic integrals. In this case, then, $\delta\alpha$ and $\delta\beta$ may have either sign; if ω be sufficiently large—we must not, of course, suppose it so large that these approximations no longer hold—both circles of latitude will now *rise* in the sphere.

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* The instability in the lowest position if ω exceeds $\sqrt{\frac{g}{a}}$ exhibits a fundamental difference that may arise in the question of stability owing to the presence of friction. See Lamb, "On Kinetic Stability," Proc. Roy. Soc. lxxx. (1908), where this is discussed and other examples are given.

3. We can show that if $\delta\alpha > 0$ then $\delta\beta < 0$, and consequently if $\delta\beta < 0$ then $\delta\alpha < 0$. For we can write

$$\delta\alpha = \mathrm{K}\int_0^{\mathrm{T}} (\cos\theta - \cos\alpha)\left[\omega\Omega_\alpha(\cos\alpha + \cos\theta) - \frac{2g}{a}\right]dt,$$

$$\delta\beta = \mathrm{K}'\int_0^{\mathrm{T}} (\cos\beta - \cos\theta)\left[\omega\Omega_\beta(\cos\beta + \cos\theta) - \frac{2g}{a}\right]dt,$$

where K, K′ are positive constants. Hence if $\delta\alpha > 0$ we must have

$$\omega > \frac{2g}{a\Omega_\alpha(\cos\alpha + \cos\beta)} = \Omega_\beta,$$

for otherwise the integrand would always be negative. Similarly, if $\omega > \Omega_\alpha$ then $\delta\beta$ is certainly positive. But $\Omega_\beta > \Omega_\alpha$, and hence the result is proved. It is easy to see, however, that if $\delta\alpha < 0$ then $\delta\beta$ may have either sign.

Since $\Omega_\alpha^2 < \frac{g}{a}\sec\alpha$, we see that if $\cos\alpha > \frac{g}{a\omega^2}$ then $\delta\beta > 0$; and similarly, if $\cos\beta < \frac{g}{a\omega^2}$ then $\delta\alpha < 0$. In other words, if the upper circle of latitude of the frictionless motion lies above the ultimate relative equilibrium position, the lower circle will be rising; while if the lower circle lies below this position, the upper circle will be falling. In particular, if $\omega^2 < \frac{g}{a}$, so that the bottom position is the only one of relative equilibrium, the upper circle will always fall, but not necessarily the lower one. We may observe that if Ω_α (and hence also Ω_β) is negative—*i. e.*, the particle is circulating in the opposite direction to the rotation of the sphere,—then $\delta\alpha$, $\delta\beta$ are necessarily negative.

As a particular case consider that in which $\Omega_\alpha = 0$, that is, in the absence of friction the motion would be in a fixed plane. In this case $\delta\alpha$ is negative, but the formula for $\delta\beta$ fails, as we would expect, for then $\beta = 0$ and $\Omega_\beta = 0$. We may then proceed as follows. Since $h_0 = 0$, h is obviously small. Hence from (13) we may write

$$h = \mu\omega\int_0^t \sin^2\theta\, dt\,; \qquad \mathrm{E} = \mathrm{E}_0(1 - 2\mu t) - \frac{2\mu g}{a}\int_0^t \cos\theta\, dt.$$

If $\theta=\epsilon$ is the lowest position in the sphere reached, we have for the energy there

$$\frac{1}{2}\frac{h^2}{\sin^2\epsilon}-\frac{g}{a}\cos\epsilon=\mathrm{E}_0(1-2\mu\mathrm{T}')-\frac{2\mu g}{a}\int_0^{\mathrm{T}'}\cos\theta\,dt,$$

where T' is $\frac{\mathrm{T}}{2}$ in the previous notation, *i. e.*, one-quarter of the complete period of a simple pendulum of angle α. Substituting for h, since $\mathrm{E}_0=-\frac{g}{a}\cos\alpha$, this gives

$$\frac{\mu^2\omega^2}{2\sin^2\epsilon}\left[\int_0^{\mathrm{T}'}\sin^2\theta\,dt\right]^2+\frac{2\mu g}{a}\int_0^{\mathrm{T}'}\cos\theta\,dt+2\mu\mathrm{E}_0\mathrm{T}'$$
$$=-\frac{g}{a}\cos\alpha+\frac{g}{a}\cos\epsilon.$$

Since on the right-hand side there is a term $\frac{g}{a}(1-\cos\alpha)$ which is not small, we can equate this to the first term on the left-hand side, giving approximately

$$\epsilon=\frac{\mu\omega}{2\sqrt{\frac{g}{a}}\sin\frac{\alpha}{2}}\int_0^{\mathrm{T}'}\sin^2\theta\,dt.$$

This gives the small deviation from the position $\theta=0$ produced by the friction. What we have previously called $\delta\beta$ is twice this.

For the "conical pendulum" case we find, corresponding to (11),

$$\delta_1\alpha=-\frac{2\pi}{p}\frac{\mu\sin 2\alpha}{\sin^2\alpha+4\cos^2\alpha}\left(1-\omega\sqrt{\frac{a\cos\alpha}{g}}\right),$$

showing that the particle ascends or descends according as ω^2 is greater or less than $\frac{g}{a\cos\alpha}$.

4. In the case where the ordinary laws of friction are assumed and the coefficient of friction is small, we can easily obtain expressions for $\delta\alpha$, $\delta\beta$, $\delta_1\alpha$ analogous to the above. They are somewhat complicated, however, and it does not seem worth while to reproduce them. In the general case, just as in the case of the fixed sphere, we see that after a finite time the particle will come to relative rest within certain regions on the sphere.

There is in any case a region of relative equilibrium below a certain circle of latitude, while if ω is sufficiently great, there is, in addition, another such region between two circles of latitude, both lying above the first-mentioned circle. In this case, since the particle can rest in relative equilibrium when displaced a small distance from the lowest position, we cannot say that this position is unstable, even if the angular velocity of the sphere is very large.

I wish to express my thanks to Professor Bartky, of the University of Chicago, who kindly gave me the benefit of his criticism during the writing of this paper.

University of Toronto.

LXVIII. *The Eleven-year and Nineteen-year Periods and other related Periods of Earthquake Frequency.* By CHARLES DAVISON, *Sc.D.*, *F.G.S.*[*]

MOST of the results of this paper are based on the late Prof. Milne's great catalogue of more than four thousand destructive earthquakes between the years A.D. 7 and 1899[†]. In estimating the intensity of the shocks, Milne used the following scale:—

1. Walls cracked, chimneys broken, or old buildings shattered.
2. Buildings unroofed or shattered and some thrown down.
3. Towns destroyed and districts desolated.

By taking 3-yearly means of the annual numbers of earthquakes of each intensity, minor inequalities in the frequency-curve are smoothed away, and the years in which earthquakes are clustered stand out clearly. These years are given in a short paper recently published[‡], and it is there shown that some of the intervals between the cluster-years are about 11 years or multiples of 11 years, and that many of the cluster-years agree closely with years of low sun-spot frequency.

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[*] Communicated by the Author.

[†] Brit. Ass. Rep. 1911, pp. 649–740.

[‡] 'Nature,' cxx. pp. 587–588 (1927).

The 11-*year Period.*

In the present paper, I have used a simple form of harmonic analysis, that gives results of sufficient accuracy considering the nature of our earthquake-catalogues *. For the 11-year period, the numbers of earthquakes in the years 1701, 1712, ..., 1888; 1702, 1713, ..., 1889; and so on, were added together, and 5-yearly means were taken of the 11 sums. By this process of taking means, the amplitude of the period is reduced and that obtained must be multiplied by the factor 1·462. In all cases, unless otherwise mentioned, the earthquakes are those of the Northern Hemisphere (2421 in number from 1701 to 1898), the records for the Southern Hemisphere (303 earthquakes) being too scanty to give results.

TABLE I.

Intensity.	Max. Epoch.	Amplitude.
3	1709	·16
2	1708	·18
1	1708-09	·09
3, 2, 1	1708-09	·12

As an 11-year earthquake-period is one of some interest, it seemed desirable to test its reality in other ways. In Table II. are given the results for different centuries; in Table III. those for different seasons; and in Table IV. those for different regions, the three intensities being grouped together in Tables III. and IV.

TABLE II.

Intensity.	Interval.	Max. Epoch.	Amplitude.
3	1701-99	1709	·39
	1801-99	1807 (1708)	·09
2	1701-99	1709	·22
	1801-99	1807 (1708)	·16
1	1701-99	1708	·04
	1801-99	1808 (1709)	·12
3, 2, 1	1701-99	1709	·15
	1801-99	1807 (1708)	·12

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* An account of the method is given in Phil. Trans. 1893 A, pp. 1108-1111.

TABLE III.

Season.	Max. Epoch.	Amplitude.
Winter (Dec.–Feb.)	1710	·19
Spring (Mar.–May)	1708	·18
Summer (June–Aug.)	1707	·20
Autumn (Sep.–Nov.)	1709	·09

TABLE IV.

Region.	Max. Epoch.	Amplitude.
Europe	1709	·15
Asia	1708	·18
Italy	1709	·20
China	1709–10	·22
Island groups of W. Pacific	1708–09	·20

The following results are of less value, owing to the comparatively small numbers of earthquakes recorded: North America, epoch 1702, amplitude ·25; Central America, epoch 1708, amplitude ·38; West Indies, epoch 1709, amplitude ·18.

The results given in Table V. are of interest, as most of the earthquakes did not reach destructive intensity.

TABLE V.

Region.	Interval.	Max. Epoch.	Amplitude.
Italy (Baratta)	1701–1898	1707–08	·12
Great Britain (Davison)	"	1708–09	·32
Switzerland (Swiss Earthq. Ser.)	1883–1926	1885 (1709)	·37
Norway (Kolderup)	1893–1925	1895 (1708)	·28
Zante (Barbiani)	1826–58	1831 (1710)	·73
Philippines (Masò)	1801–1921	1807 (1708)	·34
New Zealand (Hogben)	1868–89	1875 (1710)	·10

The 22-year Period.

With the aid of Milne's catalogue, I next tested the existence of other periods of various lengths. In addition to two or three possible periods, there are four periods of some importance, of durations 22, 33, 19, and 38 years. These were traced by taking 11-year means of the 22 sums, 17-year means of the 33 sums, 9-year means of the 19 sums, and 19-year means of the 38 sums, the augmenting factors being 1·576, 1·624, 1·501, and 1·574, respectively. The reality of these periods was tested in the same way as that of the 11-year period, except that for two periods—those of 22 and 38 years—earthquakes of intensity 1 were omitted.

TABLE VI.

Intensity.	Interval.	Max. Epoch.	Amplitude.
3	1701–1898	1716	·24
2	„	1719	·14
3, 2	„	1716	·17
3	1701–1810	1717	·27
	1789–1898	1804 (1716)	·22
2	1701–1810	1715	·25
	1789–1898	1807 (1719)	·16
3, 2	1701–1810	1716	·17
	1789–1898	1804 (1716)	·16

TABLE VII.

Season.	Max. Epoch.	Amplitude.
Winter (Dec.–Feb.)	1714	·24
Spring (Mar.–May)	1717	·13
Summer (June–Aug.)...............	1718	·30
Autumn (Sep.–Nov.)	1716	·20

TABLE VIII.

Region.	Max. Epoch.	Amplitude.
Europe	1719	·20
Asia....................................	1716	·24
Italy	1719–21	·36
China	1716	·33
Island groups of W. Pacific ...	1718–19	·25

The following results are again of less value owing to the comparatively small numbers of earthquakes: North America, epoch 1715, amplitude ·41; West Indies, epoch 1717–19, amplitude ·27.

For Italy (Baratta), the epoch was 1720 and the amplitude ·24.

The 33-year Period.

TABLE IX.

Intensity.	Interval.	Max. Epoch.	Amplitude.
3	1701–1898	1724–29	·13
2	„	1724	·29
1	„	1724	·28
3, 2, 1	„	1724	·26
3, 2, 1	1701–99	1725	·36
	1801–99	1823 (1724)	·24

TABLE X.

Season.	Max. Epoch.	Amplitude.
Winter (Dec.–Feb.)	1724	·37
Spring (Mar.–May)	1725	·21
Summer (June–Aug.)	1723	·24
Autumn (Sep.–Nov.)	1724	·29

TABLE XI.

Region.	Max. Epoch.	Amplitude.
Europe	1724	·23
Asia	1724	·31
Italy	1725	·26
Island groups of W. Pacific	1724	·41

For the destructive earthquakes of North America, Central America, and the West Indies, the epoch was 1721 and the amplitude ·28. For the earthquakes of Italy (Baratta) the epoch was 1724–25 and the amplitude ·24.

The 19-year Period.

TABLE XII.

Intensity.	Interval.	Max. Epoch.	Amplitude.
3	1701–1890	1717	·29
2	„	1715	·20
1	„	1714	·24
3, 2, 1	„	1714	·21
3	1701–95	1715	·24
	1801–95	1812 (1717)	·33
2	1701–95	1716	·26
	1801–95	1813 (1718)	·12
1	1701–95	1714	·29
	1801–95	1808 (1713)	·15
3, 2, 1	1701–95	1714–15	·23
	1801–95	1809 (1714)	·12

TABLE XIII.

Season.	Max. Epoch.	Amplitude.
Winter (Dec.–Feb.)	1717	·24
Spring (Mar.–May)	1714	·23
Summer (June–Aug.)	1714	·15
Autumn (Sep.–Nov.)	1714	·29

TABLE XIV.

Region.	Max. Epoch.	Amplitude.
Europe	1714	·23
Asia	1716	·23
Italy	1714	·11
China	1716	·39
Island groups of W. Pacific	1717	·15

For the destructive earthquakes of North America, the epoch was 1716 and the amplitude ·29. For the earthquakes of Italy (Baratta, 1701–1890), the epoch was 1714 and the amplitude ·11.

The 38-year Period.

In the following table the results are given for earthquakes of intensities 3 and 2 together, the duration of the record in each case being from 1701 to 1890:—

TABLE XV.

Region.		Max. Epoch.	Amplitude.
North Hemisphere		1724–25	·19
" "	Winter (Dec.–Feb.)	—	—
" "	Spring (Mar.–May)	1723	·31
" "	Summer (June–Aug.)	1725	·30
" "	Autumn (Sep.–Nov.)	1722	·27
Europe		1723	·17
Asia		1724	·27
Italy		1721–22	·31
China		1724	·39
Island groups of W. Pacific		1725	·24

Periodicity and Latitude.

Table XVI., in which earthquakes of intensities 3 and 2 from 1701 to 1898 are combined, shows that, in the Northern

Hemisphere, the periodicities do not depend on the latitude[*].

TABLE XVI.

Period.	North Tropics.		North Temperate Zone.	
years.	Max. Epoch.	Amplitude.	Max. Epoch.	Amplitude.
11	1708	·35	1709	·15
22	1716–17	·32	1716	·11
33	1724–25	·18	1722–24	·24
19	1715	·20	1715	·21
38	1726–28	·33	1723–24	·17

Conclusions.

(i.) In the earthquakes of the Northern Hemisphere, there are periods of 11, 22, 33, 19, and 38 years, with maximum epochs in 1709, 1716, 1724, 1715–16, and 1724–25, respectively[†].

(ii.) All over the Northern Hemisphere the maximum epoch of each period is approximately the same.

(iii.) The periods of 11, 33, and 19 years affect similarly the destructive earthquakes of each intensity. The periods of 22 and 38 years are apparently confined to destructive earthquakes of intensities 3 and 2 only.

LXIX. *High-frequency Discharges in Helium and Neon.*

By R. L. HAYMAN, *B.A.*, *D.Phil.*, *New College, Oxford*[‡].

1. THE properties of electrical discharges produced by undamped high-frequency oscillations have formed the subject of several investigations. Hulburt[§] in America, and Gutton[||] and his collaborators in France, measured the least potentials required to start these discharges in different gases, using a large range of oscillation frequency.

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[*] In the South Tropics and the South Temperate Zone, the epochs of the 11-year period are 1705 and 1703, those of the 19-year period are 1715–16 and 1706.

[†] In the Southern Hemisphere, taking the earthquakes of intensities 3 and 2 only (118 in number), the corresponding epochs are 1703, 1718, 1723, 1710, and 1715.

[‡] Communicated by Prof. J. S. Townsend, F.R.S.

[§] E. O. Hulburt, Phys. Rev. vol. xx. p. 127 (1922).

[||] C. Gutton, Journ. Phys. t. 4, pp. 420–429 (1923); also *C. R.* t. 186, p. 303 (1928).

Kirchner* and Gill & Donaldson† discovered that the potentials required to maintain these discharges were much smaller than those required to maintain direct-current discharges under similar conditions, especially when the pressure of the gas was low and the frequency of oscillation very high. Townsend and Donaldson‡ studied discharges in bulbs and cylinders, using movable external electrodes in the form of sleeves. They showed that the electric force (volts per centimetre) required to maintain the glowing column of gas, in the cylindrical tubes, was independent of the distance between the electrodes. Townsend § subsequently found that the value of this force was independent both of the amplitude of the current and of the frequency of oscillation, and he has developed a theory in agreement with these properties of the discharges.

Richards ‖ and Hiedemann ¶ have observed striated forms of discharge in hydrogen. These have been carefully examined by Hiedemann, who has also made a quantitative study of the properties of high-frequency discharges in hydrogen and a qualitative study of the discharge phenomena in air, oxygen, nitrogen, argon, etc.

In the present paper I propose to describe some measurements of the potentials required to start and maintain high-frequency discharges in helium and neon in cylindrical tubes. The principal object of the experiments was to determine the changes in the potentials due to changes in the pressure of the gas, and in the diameter of the tube, for oscillations of different wave-lengths.

2. The arrangement of the apparatus for purifying the helium and neon was the same as that described in the accounts of other researches which were made in this laboratory **. Traces of hydrogen were removed by passing the gas over copper oxide at a dull red heat, and other impurities were absorbed by keeping the gas in a tube containing charcoal, which was cooled by liquid air. Suitably placed liquid-air traps prevented contamination by mercury vapour from the McLeod gauge or evacuation

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* F. Kirchner, *Ann. der Phys* lxxvii. (3) p. 287 (1925).

† E. W. B. Gill and R. H. Donaldson, Phil. Mag. ii. p. 129 (1926).

‡ J. S. Townsend and R. H. Donaldson, Phil. Mag. v. p. 178 (1928).

§ J. S. Townsend, *C. R.* t. 186, p. 55 (Jan. 1928).

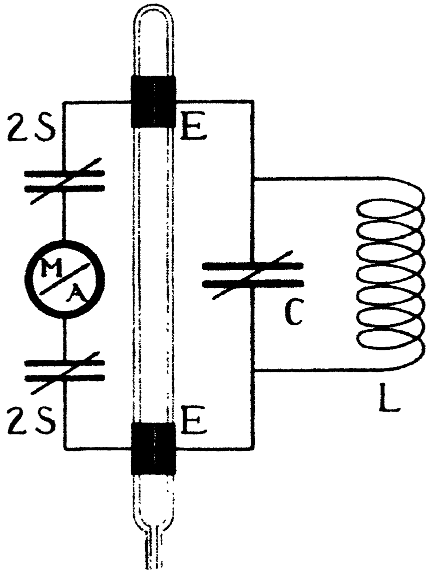
‖ R. C. Richards, Phil. Mag. ii. p. 508 (1926).

¶ Hiedemann, *Ann. der Phys.* lxxxv. p. 43 (1928).

** J. S. Townsend and C. M. Focken, Phil. Mag. ii. p. 474 (1926); L. G. Huxley, Phil. Mag. v. p. 721 (1928) pumps. The purity of the gas could be tested by a spectroscopic examination of the high-frequency discharge, using a direct-vision spectroscope.

3. The discharge-tubes were cylindrical, and were fitted with movable external electrodes. The tubes were thoroughly baked out before use, and were frequently re-heated in the course of the experiments. This was done while they contained some helium or neon, which was pumped out while the tubes were still hot. Any impurities given off by the walls were thus removed. One tube was made of quartz and the others of pyrex. It was possible to bake out the quartz tube at a much higher temperature than the pyrex tubes. The results of the experiments on the measurements of potentials of discharges in quartz and pyrex tubes were exactly the same when all the tubes had been heated to as high a temperature as possible for many hours.

Fig. 1.



4. The electrical arrangements for measuring the potentials were similar to those developed by Townsend and Donaldson. The source of high-frequency oscillations was a 60-watt valve generator. This was loosely coupled to the coil L (fig. 1)

of an oscillatory circuit (L : C and S) tuned approximately to resonance. The electrodes (E) in the form of lead sleeves, 4 cm. long, fitting closely to the surface of the tubes, were connected to the ends of the coil (L). The amplitude of the potential between the electrodes could be measured in terms of the current passing through the two equal condensers (2 S) shunted across the main tuning condenser (C).

The measuring instrument was a low-resistance thermal ammeter reading from 10 to 100 milliamps. It was connected between the two condensers (2 S), and it was therefore at a potential node. This ensured that its readings were unaffected by its capacity to earth.

5. The radial distribution of luminosity in the discharge depends on the pressure of the gas and the current flowing between the electrodes. The ratio of the intensity near the axis to that near the walls of the tube is greatest at high pressure and in weak discharges, and it appears to increase with the wave-length of oscillation.

The colour of the discharge varies with the pressure of the gas and the intensity of the electric field. When the pressure of the gas is high and the field-strength low, the lines towards the red end of the spectrum seem to be the strongest. The result of decreasing the pressure or increasing the electric field is to shift the region of maximum intensity towards the blue end of the spectrum. Thus the colour of the discharge in neon at 80 mm. pressure is orange under the electrodes where the electric force is strong, and bright red throughout the rest of the tube. At $\frac{1}{3}$ mm. pressure the ratio of the electric force to the pressure is greater, and the discharge is yellow throughout.

6. The potentials required to start and to maintain these discharges depend on several factors, of which the following are the most important:—The nature, purity, and pressure of the gas, the distance between the electrodes, the diameter of the discharge-tube, and the wave-length of the oscillations. Measurements of the smallest potentials required to start discharges could be repeated to an accuracy of 3 or per cent. under a given set of conditions. A higher degree of accuracy was obtainable in measuring the smallest potentials required to maintain a small current with a uniform glow throughout the whole length of the tube, between the electrodes.

In this paper these potentials will be referred to as the starting and the maintenance potentials.

Such variations as were observed were always greater when the distance between the electrodes was large than when it was small.

7. Quantities of impurity too small to be easily detected spectroscopically produced a marked effect on the starting potential. Thus a pyrex tube which had only received a few hours' heating was filled with pure neon, and the starting potentials were measured. A small area of the tube was heated with a blow-pipe until the glass began to soften. In the course of this heating the colour of the discharge changed from red to blue, owing to the evolution of water-vapour, hydrogen, and other impurities. The tube was then allowed to cool, and the starting potentials were again measured with the same gas, which contained a small amount of impurity. The potentials were found to be smaller than those obtained when the gas was pure, even though the discharge had practically regained its original colour. The spectrum was then examined, and an extremely faint background due to impurities was observed.

The results of these experiments are given in Table I., where the amplitudes of the potentials are given in volts.

TABLE I.

Neon at 2·55 mm. pressure (measured before and after the tube had been heated).

Tube: Pyrex 3·9 cm. diameter. Wave-length 80 metres.

Distance between electrodes.	Starting Potentials before heating.	Starting Potentials after heating.
3 cm.	232	198
6 „	357	344
9 „	490	463
12 „	566	518

The experiment was repeated, using helium in the place of neon, and the results obtained were exactly similar. In both gases the lowering of the maintenance potentials, resulting from the introduction of the impurity, was much less than the lowering of the starting potentials, and was too small to be determined with any degree of accuracy. This is attributable to the removal of impurities from the gas, by the passage of the discharge, in the manner described by Townsend and MacCallum *.

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* J. S. Townsend and S. P. MacCallum, Phil. Mag. v. p. 695 (1928).

8. The starting potentials of discharges in pure helium and neon were measured over a large range of pressures. It was found that there corresponds to each distance between the electrodes a certain pressure at which the starting potential is a minimum. The value of the potential at this minimum increases with the distance between the electrodes. The results of measurements of the starting potentials of discharges in a quartz tube 2·9 cm. in diameter are given in Table II., in which the starting potentials are given in terms of the pressure p and the distance x between the inner edges of the electrodes. The wave-length used was 80 metres.

Table II.

Starting Potentials in terms of p and x in Neon and Helium.

	Neon.		Helium.	
p. in mm.	x=3 cm. Volts.	x=6 cm. Volts.	x= 3 cm. Volts.	x=6 cm. Volts.
0·25	242	260	—	—
0·5	222	285	320	320
1·0	210	322	225	350
2·0	230	380	245	400
4·0	290	455	285	480
8·0	385	570	345	590
16·0	485	740	440	755
32·0	490	880	-	—

9. Experiments were also made with tubes of different sizes. It was found that the greater the diameter of the tube the smaller the starting potential: for example, measurements were made using tubes of 1·5, 2·9, and 3·9 cm. diameter (when the electrodes were 3 cm. apart). The starting potentials in the 1·5-cm. tube exceeded those in the 3·9-cm. tube by an amount which was small at high pressures (not more than 20 per cent. at 30 mm.), but which increased as the pressure was lowered, and reached as much as 100 per cent. at about 1 mm.

10. The starting potentials were also determined for oscillations of different wave-lengths from 40 and 640 metres. Between these limits the potentials increase with the wave-length. The results of the experiments with the tube 2·9 cm. diameter are given in Table III. for wave-lengths (λ) of 40, 80, 160, and 320 metres, and pressures (p) from ·1 mm. to

6 mm. At higher pressures the starting potential was approximately the same for all wave-lengths. The distance between the inner edges of the electrodes was 6 cm. in these experiments.

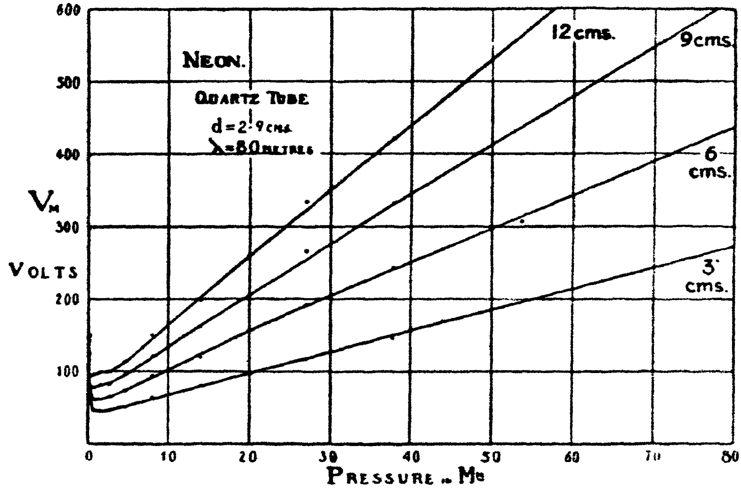
Table III.

Showing Variation in Starting Potential due to change of Wave-length.

Neon.

	λ.			
p, in mm.	40 metres. Volts.	80 metres. Volts.	160 metres. Volts.	320 metres. Volts.
0·11	179	340	1000	1150
0·24	228	259	428	510
0·54	258	283	338	384
1·2	320	335	362	376
2·5	400	403	410	421
6·1	510	510	526	520

Fig. 2.

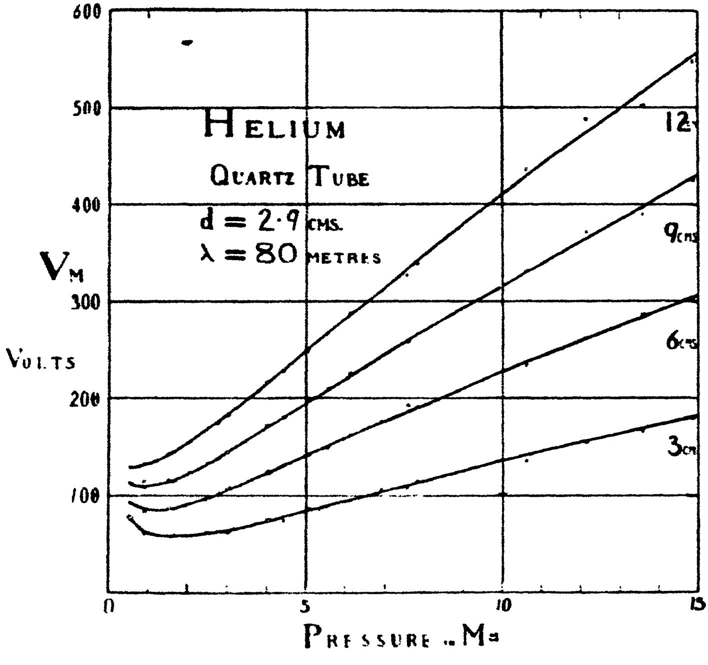


11. The potential required to maintain a discharge varies with the current. There is a certain current i_m for which the potential has a minimum value V_m. The current at this point is slightly greater than the least current which gives a uniform glow in the tube. The current i_m appears to be independent of the distance between the electrodes. The

corresponding potentials V_m between the electrodes can be readily measured.

The results of the experiments made with a tube 2·9 cm. in diameter containing neon at various pressures are given by the curves (fig. 2), the wave-length of the oscillations being 80 metres. In this diagram the ordinates represent the amplitudes of the potentials V_m in volts, and the abscissæ the pressure of the gas in millimetres. The four curves correspond to the distances 3, 6, 9, and 12 cm. between the electrodes.

Fig. 3.



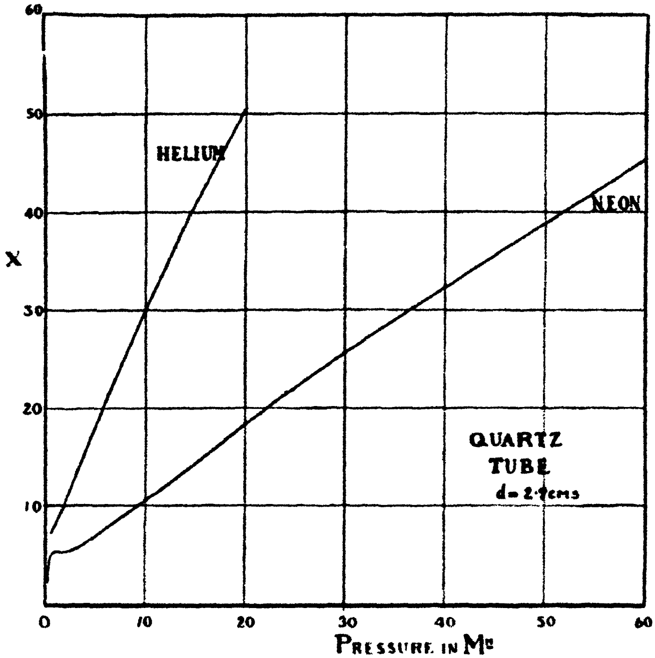
The results of similar experiments with helium are given by the curves (fig. 3).

With each gas there is a certain value of the pressure for which V_m has a minimum value.

For higher pressures the potential increases with the pressure by amounts which are approximately proportional to the increases of the pressure, as is seen by the curves, which are approximately straight lines for the larger values of p.

An important characteristic of these discharges is that equal increases in the distance (x) between the electrodes result in equal increases in the potential. Thus the electric force $X = \frac{V_m - V_m'}{x - x'}$ in the central part of the tube is independent of the distance between the electrodes, as was observed by Townsend and Donaldson. The magnitude of this force depends on the pressure of the gas, and this is shown by the curves in fig. 4, where the ordinates give the amplitudes of the force X in volts per centimetre, and the abscissæ the pressure in millimetres. The values of X were found to be independent of the wave-length of the oscillations within the range from 40 to 640 metres.

Fig. 4.



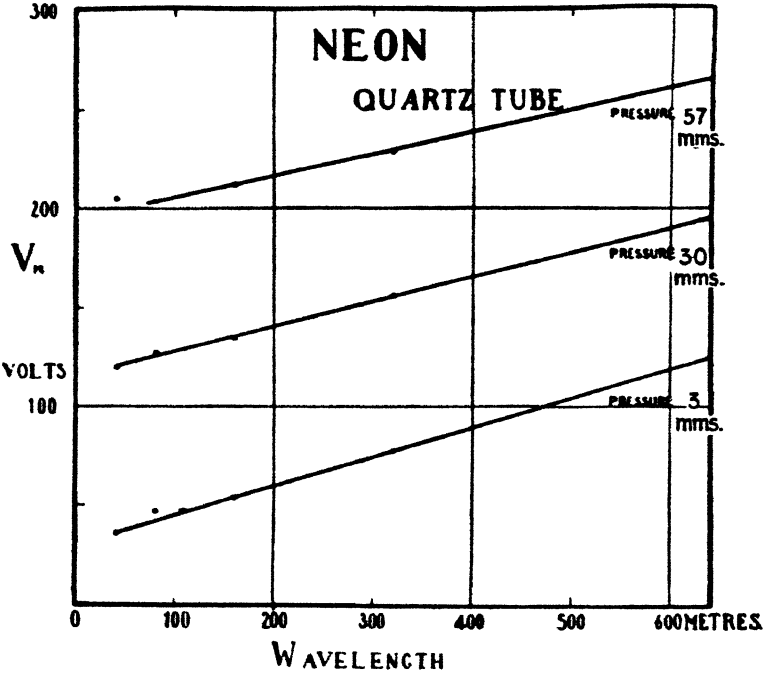
12. The maintenance potentials vary considerably with the wave-length, which shows that the potential between the electrodes consists of two parts.

The first is the fall of the potential in the central column of the gas, in which the electric force is uniform. This potential is independent of the wave-length, and is equal to the product of the electric force X and the effective length of the discharge *.

The second is the drop of potential at the electrodes, which is practically independent of the length of the discharge, and is roughly proportional to the wave-length.

In fig. 5 is shown the variation of the maintenance potentials with the wave-length in neon. The three curves refer to three different pressures : 3, 30, and 57 mm. The ordinates represent the amplitudes of the potentials in volts, and the abscissæ the wave-lengths. The diameter of the tube was 2·9 cm., and the electrodes were 3 cm. apart.

Fig. 5.



13. Both the maintenance potentials (V_m) and the electric forces X are greater in narrow tubes than in wide tubes. The values of these quantities for three tubes containing

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* The effective length of the discharge exceeds the distance between the inner edges of the electrodes by an amount which depends on the diameter of the tube. In the 2·9-cm. tube this amount is about 1·4 cm. This can easily be verified from figs. 2 and 3.

helium at various pressures p are given in Table IV., where V_m is the amplitude of the force in volts per cm., p the pressure in millimetres, and x the distance between the electrodes in centimetres.

TABLE IV.

Helium. $\lambda = 80$ metres.

		Tube 1·5 cm. diameter.		Tube 2·9 cm. diameter.		Tube 3·9 cm. diameter.	
p, in mm.	x, in cm.	V_m.	X.	V_m.	X.	V_m.	X.
1·0......	3	148·0	10·3	60·5	8·8	46·0	7·0
,, ...	9	210·0		113·3		87·8	
2·5......	3	95·0	17·5	63·0	11·8	58·0	10·7
,, ...	9	200·0		134·0		122·0	
10·0......	3	138·0	34·7	134·0	30·7	130·0	29·8
,, ...	9	346·0		318·0		309·0	
15·0......	3	183·0	45·3	185·0	42·5	187·0	41·3
,, ...	9	455·0		440·0		435·0	

14. Some experiments were made with ionizing radiations (such as ultra-violet light and Röntgen rays from external sources) falling on the discharge-tube, but there was no appreciable effect observed.

Stable striated forms of discharge have been observed in both helium and neon. Their occurrence seems to be favoured by the use of large discharge currents, narrow tubes, long wave-lengths, and certain conditions of pressure.

When using a wave-length of 80 metres and a tube 2·9 cm. in diameter, striations were only observed in helium at pressures exceeding about 12 mm., and in neon at pressures less than 2 mm.

The striated form of discharge in helium was similar to that observed in hydrogen, and consisted of a series of pairs of luminous disk with their planes perpendicular to the direction of the electric force. The striated discharge in neon consisted of a series of luminous ovals equally spaced along the axis of the tube.

My best thanks are due to Professor Townsend for his advice and the interest he has taken in this work.

LXX. *The Raman Effect in some Organic Liquids.*

By S. Venkateswaran[*].

[Plate XV.]

I. *Introduction.*

THE recent discovery by Prof. Raman[†] of a new type of secondary radiation offers an entirely new and very accurate and convenient method for measuring the infra-red frequencies of transparent media. It has been found by him that when monochromatic light is diffused by a liquid, the scattered light ceases to be monochromatic and several new lines and sometimes bands appear in the scattered spectrum. The difference in frequency between the incident line and a modified line generated by it gives a natural frequency of the molecule. In a single photograph the modified lines corresponding to all the infra-red frequencies can thus be obtained and measured accurately, the degree of accuracy being limited only by the width of the line. In this paper the characteristic infra-red frequencies of some fatty acids have been determined by this method and their values given.

II. *Experimental Methods.*

The experimental arrangements were similar to those described by Raman and Krishnan[‡] and by the author[§] in their recent papers. Kahlbaum's acetic acid and Merck's extra pure propionic and butyric acids were further purified by repeated slow distillation *in vacuo* in large double bulbs. The bulb containing the purified liquid was immersed in a glass tank containing water, and light from a 3000 c.p. mercury arc lamp was condensed into the liquid with an 8-inch condenser. The spectrum of the transversely-scattered light was taken with a Hilger E 2 quartz spectrograph.

The plates were measured with a Hilger travelling micrometer, and the wave-lengths of the modified lines were calculated, taking the mercury arc lines as standards. The simplified Hartmann interpolation formula was used.

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[*] Communicated by the Author.

[†] C. V. Raman, "A New Radiation," Ind. Journ. Phys. vol. ii. p. 387 (1928). See also C. V. Raman and K. S. Krishnan, 'Nature,' vol cxxi. p. 501 (31st March, 1928).

[‡] C. V. Raman and K. S. Krishnan, "A New Class of Spectra due to Secondary Radiation," Ind. Journ. Phys. vol. ii. pt. iv. p. 399 (1928).

[§] S. Venkateswaran, "Study of Raman Effect in Glycerine and Glycerine Water Mixtures," Ind. Journ. Phys. vol. iii. pt. i. p. 105 (1928).

III. *Results.*

The spectrograms of the light-scattering in acetic, propionic, and butyric acids are reproduced in figs. 2, 3, and 4 (Pl. XV.). (Fig. 1 represents the corresponding incident spectrum.) All the modified lines have been analysed, and the difference in wave-numbers between each of the exciting and its corresponding modified lines have been calculated. The characteristic infra-red frequencies thus obtained and their wave-lengths are given in Table I.

The modified lines corresponding to 7·0 μ and 3·4 μ broaden into a band as we go up the series. In fact, the band shows a fine structure which is, however, not well resolved in the instrument. The intensity of the modified line due to 16·0 μ rapidly diminshes from acetic to butyric acid.

The infra-red absorption spectrum of acetic acid has been studied by Coblentz, and that of butyric acid by Weniger [*]. A comparison of their values with those obtained by the author is given in Table II.

The agreement between the values calculated from light-scattering and those obtained directly from infra-red measurements must be considered good. Of the various characteristic frequencies of the molecules of the fatty acids, the one corresponding to 3·4 μ has been identified as corresponding to the C–H bond, and that corresponding to 7·3 μ as arising from the O–H group.

An examination of the spectrograms reproduced in the paper shows that all the modified lines are rather broad and diffuse in the fatty acids, unlike those observed in benzene, toluene, carbon tetrachloride, and other liquids. In addition to the modified lines, there is a continuous spectrum. That the presence of the continuous spectrum is characteristic of the liquids and not due to any impurities, is shown by the fact that it is observable in these liquids, even after the most careful purification. An inter-comparison of the spectrograms shows that the intensity of the continuous spectrum is of the same order in acetic and propionic acids, but is appreciably larger in butyric acid. In his study of the Raman effect in glycerine the author has shown that the presence of the continuous spectrum, which is so prominent in this liquid, is connected with its high viscosity. On the basis of this hypothesis, the larger intensity of the continuous spectrum in the scattered light in butyric acid is easily understood in view of its higher viscosity.

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[*] See W. Weniger, Physical Review, xxxi. p. 388 (1910).

TABLE I.

Acetic acid.	Shift in wave-number.	446	623	766	908	...	1128	1280	1364	1433	1670	2944
		(½)	(5)	(0)	(5)		(0)	(3)	(3)	(3)	(2)	(4)
	Wave-length in μ ...	22·41	16·05	13·05	11·01	...	8·86	7·81	7·33	6·98	5·99	3·396
Propionic acid.	Shift in wave-number.	485	608	770	860	1040	1134	1275	1370	1443	1664	2955
		(0)	(½)	(½)	(4)	(0)	(3)	(1)	(½)	(4)	(1)	(3)
	Wave-length in μ ...	20·61	16·44	12·98	11·62	9·61	8·81	7·84	7·30	6·93	6·01	3·383
Butyric acid.	Shift in wave-number.	...	...	778	869	1044	1125	...	1364	1439	1659	2941
				(½)	(2)	(½)	(1)	...	(1)	(½)	(½)	(2)
	Wave-length in μ ...	...	...	12·85	11·50	9·58	8·88	...	7·33	6·97	6·02	3·399

Note.—The numbers within brackets indicate the relative intensities of the modified lines.

TABLE II.

Acetic acid.	Wave-length in μ (author).	22·41	16·05	13·05	11·01	...	8·86	7·81	7·33	6·98	5·99	3·396
	„ „ (Coblentz).	...	...	12·9	11·0	...	8·9	...	7·2	...	5·9	3·5
Butyric acid.	Wave-length in μ (author).	...	...	12·85	11·50	9·58	8·88	...	7·33	6·97	6·02	3·399
	„ „ (Weniger).	...	...	12·9	10·6	9·3	...	...	7·1	...	5·9	3·6

Summary.

1. The infra-red frequencies of acetic, propionic, and butyric acids have been measured from the Raman lines. The values for acetic and butyric acids agree closely with those obtained by Coblentz and Weniger. Some characteristic frequencies have been measured in the extreme infra-red region not accessible to their infra-red spectrometers.

2. The spectrum of light-scattering in the three acids shows the presence of the modified lines and a continuous spectrum. The intensity of the latter is nearly the same in acetic and propionic acids, but is appreciably larger in butyric acid. This larger intensity of the continuous spectrum is probably due to the higher viscosity of butyric acid.

The author desires to express his thanks to Prof. C. V. Raman, F.R S., for his kind guidance, and to Mr. K. S. Krishnan for his kind interest in the work.

210 Bow Bazar Street,
Calcutta.
September 6th, 1928.

LXXI. *High Frequency Discharges in Gases.* By J. S. Townsend, *M.A., F.R.S., Wykeham Professor of Physics, Oxford, and* W. Nethercot, *B.A., Merton College, Oxford* [*].

1. In order to investigate certain properties of high frequency discharges in gases, it is convenient to use long cylindrical tubes with external electrodes in the form of sleeves which may be placed at different distances apart. By this means the potentials required to start electrodeless discharges have been measured, and also the minimum potential required to maintain the minimum current which gives a uniform glow in the tube [†].

The investigations have been extended in order to determine the potentials required to maintain currents of different amplitudes, which give a uniform glow in the tube. With these currents the potential increases with the current, but for a given current the rate of increase of the potential with the distance between the electrodes is a constant, which is the same over a large range of currents and over a large range of frequencies of oscillation.

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[*] Communicated by the Authors.

[†] J. S. Townsend and R. H. Donaldson, Phil. Mag. v. p. 178 (Jan. 1928).

This result, which was first obtained with tubes containing helium and neon, formed the basis of a theory [*] of the uniform glow in an electrodeless discharge.

The theory indicates that the mean value of the electric force in the glow of a high frequency discharge should be the same as the force in the uniform positive column of a continuous current discharge.

2. The condition that a continuous current in a gas shall be maintained by a given field of force may be expressed in the form of a relation between the coefficients of ionization α and β which is independent of the intensity of the current [†]. Thus the potential is independent of the intensity of the current when the field of force is not disturbed by the current. This condition is obtained with small currents, since the charge in the gas (due to an excess of positive ions or electrons) is small and the field of force is not disturbed to any great extent. The charge in the gas increases with the current, and generally with large currents the field of force is altered and the force may become distributed so as to facilitate the discharge, as with currents between parallel plate electrodes, or the force may be distributed so as to impede the current as in the corona discharge. In these cases the charges which disturb the field are accumulated in the spaces near the electrodes.

3. At points in the gas remote from the electrodes the charge in the gas may be independent of the current, even when comparatively large currents are flowing. In these cases the electric force is independent of the current, provided the density of the gas in the path of the discharge is not changed to any great extent by the increase of temperature due to an increase of current.

The uniform positive column of a continuous current discharge in a long tube is an example of a space where the charge in the gas and the electric force parallel to the axis of the tube are constant over a large range of currents. The force parallel to the axis has been determined by Wilson over wide ranges of the currents. In air at pressures less than 1 mm. he found that the force was nearly constant, but at higher pressures the force diminishes as the current increases. The experiments were made with a tube 2·1 mm. in diameter, and with air at 2·81 mm. pressure the force was independent of the current with currents from 10^{-4} to 10^{-3} ampere, but the force changes from 57 to 54 volts per cm. when the current is increased from $4{\cdot}05\times10^{-3}$ ampere to $7{\cdot}8\times10^{-3}$ ampere *.

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[*] J. S. Townsend, *Comptes Rendus*, clxxxvi. p. 55 (Jan. 1928).

[†] 'Electricity in Gases,' section 293.

4. We have obtained similar results in our experiments with high frequency discharges in nitrogen. With small currents the force in the uniform glow in the high frequency currents is constant, but with large currents the force changes with the current. The change of force with the current is much smaller in wide tubes [3 or 4 cm. in diameter] than in narrow tubes. This indicates that the change of force is probably due to the increase of temperature obtained with the large currents. An increase of temperature in the path of the discharge reduces the density of the gas, and a smaller force is required to maintain the current, since the force diminishes with the pressure when the temperature is constant.

In the positive column the ratio of the electric force to the pressure of the gas is small, and it may be assumed that positive ions do not ionize molecules of the gas, and that the current is maintained by the process of ionization due to collisions of electrons with molecules of the gas. The electric force is determined by the condition that the supply of ions due to this process is balanced by the loss due to diffusions to the sides of the tube. The theory formed on this hypothesis shows that there must be a positive charge in the gas which repels positive ions towards the surface and retards the rate at which electrons reach the surface by diffusion, so that the positive ions reach the surface at the same rate as electrons.

Thus the number of positive ions n_2 per cubic centimetre exceeds the number of electrons n_1, but the excess (n_2-n_1) is small compared with n_2 or n_1, and the charge $e(n_2-n_1)$ is independent of n_1 or n_2. It is also necessary to assume that the effect of recombination of electrons and positive ions may be neglected, as is generally the rule in discharges at low pressures †.

Thus there are two forces in the positive column : the force parallel to the axis, which is the force that has been determined experimentally, and a force along the radius due to

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* H. A. Wilson, Proc. Camb. Phil. Soc. ix. pp. 249 & 391 (1902).

† 'Electricity in Gases,' section 302.

the charge $e(n_2-n_1)$ per c.c. of the gas. This charge has the effect of increasing the conductivity of the gas, since it reduces the rate at which electrons are lost by diffusion to the surface of the tube. There is also a charge on the inner surface of the tube which tends to become distributed so that the force along the axis is the same at all points of the uniform glow. This distribution on the surface of the tube regulates itself in the same way as the charge on the surface of a wire, which makes the electric force to be the same at all points when a continuous current is flowing in the wire.

5. On these principles a satisfactory explanation may also be obtained of phenomena which occur in the high frequency discharges in tubes with external electrodes. In the theory of these discharges which has recently been proposed, the charge $e(n_2-n_1)$ per unit length of the tube (which is independent of the current) is given in terms of the coefficients of diffusion and the mobilities of the positive ions and the electrons, and the coefficient of ionization.

The charge in the gas does not vary with the changes in direction of the oscillatory force parallel to the axis, so that the electric force along the radius is not oscillatory.

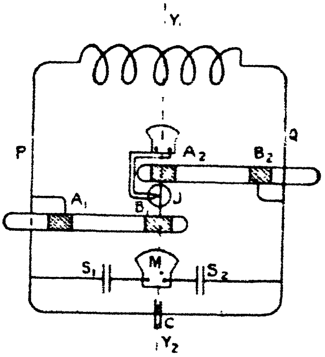
The results of the investigation are consistent with the hypotheses :—that the coefficient of ionization α with large currents of the order 10^{-3} to 10^{-2} ampere is the same as that found with small photo-electric currents ; the rate at which the electrons and positive ions are thus generated is the same as the rate at which they reach the sides of the tube ; the rate of recombination of positive ions with electrons in the gas is very small, and the loss of conductivity due to this process may be neglected.

6. This paper contains an account of the methods that have been used to determine the relation between the current and the electromotive force in high frequency discharges. Most of the experiments were made on high frequency discharges in nitrogen, but some experiments were also made with continuous current discharges in this gas, with a view to determining the electric force in the uniform positive column, with tubes of the same diameter and containing gas at the same pressure as in the experiments with high frequency oscillations. The results show that there is an agreement between the values obtained for the forces in the continuous and high frequency discharges as indicated by the theory.

The nitrogen used in these experiments was prepared by heating pure sodium azide. The discharge-tubes were evacuated to a very low pressure and heated in order to expel impurities from the surface of the glass. The tubes were then filled to a pressure of about 10 mm. with pure nitrogen, and the gas was pumped out so as to remove the impurities. This process was repeated several times, and the spectrum of an electrodeless discharge in the tubes was examined with each specimen of the gas. After the tubes had been washed out with pure gas three or four times, there were no lines due to impurities which could be seen with a direct-vision spectroscope.

When this stage was reached the tubes were allowed to cool, and were filled with nitrogen at the pressures required in the experiments on the determination of the high frequency forces.

Fig. 1.



In most of these experiments the discharges were maintained by connecting the external electrodes to a secondary circuit which was loosely coupled with a continuous wave generator. The generators which were used were of the ordinary types where the wave-length is adjusted by changing the capacity of the oscillating circuit and the amplitude of the oscillation is adjusted by changing the heating current in the filaments of the valves. Small continuous changes of amplitude are thus obtained by means of a rheostat in the circuit connecting the filament with the low tension battery. Low-power transmitting valves were generally used with a low tension battery of 6 volts to heat the filaments, and a direct current generator of 800 volts to charge the anodes.

7. Experiments were made with several arrangements of the secondary circuit, and the symmetrical form which is shown in fig. 1 was found to be the most convenient and the

most accurate for determining the current through the tube and the electromotive force between the electrodes. With this arrangement two discharge-tubes of the same dimensions and containing gas at the same pressure are required. The electrodes were in the form of sleeves A_1B_1 and A_2B_2, which could be fixed at various distances apart.

The same current flows through the two tubes and through the heater of the thermojunction J, which is connected by short wires to the sleeve B_1 of one tube and the sleeve A_2 of the other. The current through the tubes is indicated by the microammeter I, which is connected to the thermojunction.

The circuit is symmetrical with respect to the plane through the line Y_1Y_2 with the axis of the inductance normal to the plane, and points in this plane remain at zero potential while the oscillatory current flows through the circuit. Thus the thermojunction and the microammeter are in positions of zero potential, and the positions of the sleeves B_1 and A_2 may be adjusted so that there is no current in the indicator when an oscillatory current flows in the circuit and the potentials at the sleeves A_1 and B_2 are not sufficiently high to start a luminous discharge in the tubes.

When the potentials are increased a discharge is obtained, and the current through the tubes is indicated by the microammeter.

8. The potentials at the sleeves A_1 and B_2 are measured by the current in the milliammeter M which connects the plates of the adjustable condensers S_1 and S_2. These condensers were of small capacity, ranging from 15 to 120 cm., and were carefully calibrated. The capacities were adjusted to the same value S, which may be chosen so as to obtain a convenient deflexion in the milliammeter. The condensers were contained in metal cases which were connected together, both sets of plates in the condensers being insulated from the cases. A third adjustable condenser C was also used in order to bring the capacity of the circuit $(C+S/2)$ near to the point of resonance with the generator.

A current of any required amplitude was obtained through the tubes by adjusting the capacity C or by the rheostat which controlled the intensity of the oscillations in the generator.

The distance x between the sleeves A_1 and B_1, and A_2 and B_2, was adjusted by having flexible connexions to A_1 and B_2. The sleeves were 4 cm. long, and were made to fit closely to the tubes.

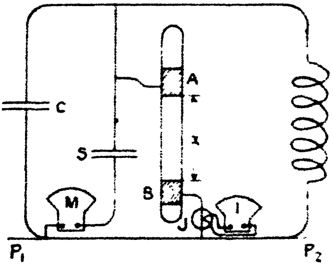
The electromotive force between the sleeves is obtained from the current M in the milliammeter by the formula $E=M/p\,.\,S$, where $p/2\pi$ is the frequency of the oscillations, $E\sqrt{2}$ being the amplitude of the electromotive force and $M\sqrt{2}$ the amplitude of the current.

9. Another arrangement of the secondary circuit which was used with single tubes in shown in fig. 2. In this case a large metal sheet P_1P_2 was used as a surface of zero potential, and the two measuring instruments were placed on the sheet.

The lower sleeve B of the discharge-tube was connected by short wires through the heater of a thermojunction J to the sheet P_1P_2, and the current through the tube was indicated by the microammeter I.

One set of plates of the adjustable condenser S was connected through the low resistance milliammeter M to P_1P_2, so that the electromotive force between the sleeves A and B is given by the formula $E=M/S\,.\,p$. As in the first arrangement, the capacity S was adjusted to give a suitable deflexion in the milliammeter, and the condenser C was used to bring the circuit into resonance with the generator. With this arrangement it was necessary to screen the microammeter and the sleeve B by conductors connected to P_1P_2, so as to have no induced current in the indicator before the current starts to flow in the tube.

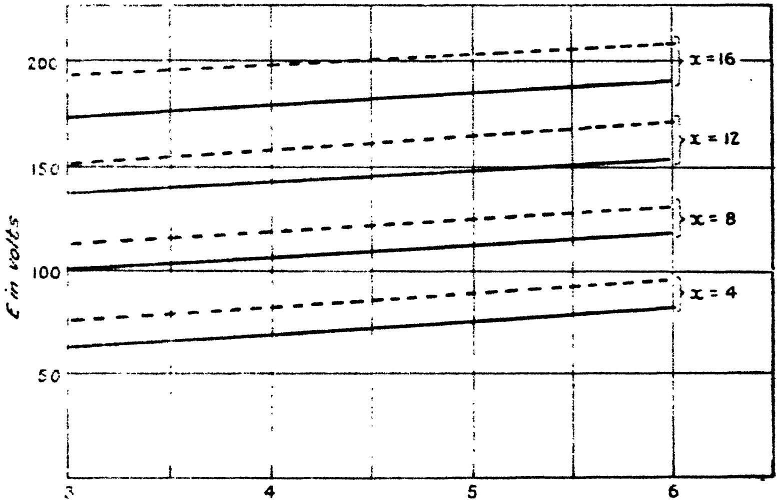
Fig. 2.



In these experiments the heater of the thermojunction was a very fine wire of high resistance, as it was not required to carry currents exceeding one-fiftieth of an ampere. With oscillations of the wave-lengths that were used, the resistance does not differ by 1 per cent. from the direct current resistance, which was of the order of two ohms. Under these conditions, accurate measurements of the high frequency currents are obtained by calibrating the microammeter with a continuous current flowing through the heater of the thermojunction.

10. The circuit (fig. 1) was used with a pair of pyrex tubes 3·9 cm. in diameter containing nitrogen at ·26 mm. pressure. The results of the experiments are shown by the four continuous curves (fig. 3), where the ordinates are proportional to the potentials, and the abscissæ proportional to the currents, the wave-length of the oscillations being 40 m. In these diagrams the root mean square value of the potential E is given in volts and the current I in milliamperes, so that

Fig. 3.



Current-electronic-force curves for nitrogen at ·26 mm. pressure, λ=40 metres.
Continuous curves refer to tube 3·9 cm. diameter.
Dotted curves refer to tube 2·9 cm. diameter.

the amplitude of the potential is $E\sqrt{2}$ and the amplitude of the current $I\sqrt{2}$.

The four curves correspond to the distances 4, 8, 12, and 16 cm. between the sleeves.

A similar set of experiments was made with the same pair of tubes, with the wave-length of the oscillations increased to 75 m. It was found that the rate of increase of E with the distance between the electrodes was the same as with 40 m., but the rate of increase of E with the current was greater in the proportion of 75 : 40.

The values of E (in volts) obtained in these experiments may be expressed in terms of the distance x between the electrodes (in centimetres), the current I in milliamperes, and the wave-length λ in metres, by the formula :

$$E = 8{\cdot}9 \times x + {\cdot}14 \lambda I + 11.$$

Table I. gives examples of the value of E obtained experimentally, and the values given by the formula for different values of x, λ, and I.

TABLE I.

Nitrogen ·26 mm. pressure. Tube 3·9 cm. in diameter.

x.	I.	E expt.	E formula.	
4	3	64	63	
8	5	111	110	$\lambda = 40$
12	4	141	140	
16	6	191	187	
4	2	71	68	
8	5	138	135	$\lambda = 75$
12	4	161	160	
16	6	212	217	

With a tube 2·9 cm. in diameter containing nitrogen at the same pressure [·26 mm.] the electromotive force is given by the formula :

$$E = 9{\cdot}5 \times x + {\cdot}17 \lambda I + 11.$$

The value of E, for oscillations 40 metres wave-length, obtained with this tube are given by the four dotted curves (fig. 3) for the distances 4, 8, 12, and 16 cm between the electrodes.

11. In general the electromotive force E is given as the sum of two terms in the form:

$$E = X(x + a) + b\lambda I,$$

where a, b, and X are constants depending on the pressure of the gas and the diameter of the tube.

The coefficient X (which represents the electric force parallel to the axis of the tube at points remote from the electrodes) depends on the pressure of the gas, but it is independent of the intensity of the current or the wave-length of the oscillations.

The term $b\lambda I$ represents an electromotive force in the spaces near the electrodes where the charges in the gas impede the current. It includes potential differences between the sleeves and the inner surfaces of the tubes, and potential differences in the gas near the electrodes where the electric force differs from the value dE/dx.

There is no important term in the expression for E involving both I and x, since dE/dx is independent of I and dE/dI is independent of x. The experiments therefore indicate that the total electromotive force may be expressed as the sum of two potentials in series (represented by the two terms in the expression for E) which are approximately in the same phase.

12. The changes in the coefficients a, b, and X with the pressure are seen by comparing the values of E, obtained with a tube 3·1 cm. internal diameter containing nitrogen at ·53 mm. pressure, with the values of E for the same tube with nitrogen at the pressure ·26 mm. With the gas at ·53 mm. pressure the values of E are given by the formula:

$$E = 13{\cdot}7\,(x+4) + {\cdot}21\,\lambda I,$$

and with the pressure at ·26 mm.:

$$E = 9{\cdot}4\,(x+1) + {\cdot}165\,\lambda I.$$

Thus the electric force X increases from 9·4 volts per cm. to 13·7 volts per cm. when the pressure is increased from ·26 mm to ·53 mm.

These values of X may be compared with the results of the earlier experiments on the force in the uniform positive column of a continuous discharge. In nitrogen at 1 mm. pressure in a tube 2·5 cm. in diameter the value of X found by Herz[*] was 26·9 volts per cm. Since the force diminishes when the pressure is reduced or the diameter of the tube increased, the value 13·7 volts per cm. obtained in a high frequency discharge with a tube 3·1 cm. in diameter containing nitrogen at ·53 mm. pressure may be considered to be consistent with Herz's determinations.

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[*] A. Herz, *Wied. Ann.* liv. p. 244 (1895).

This, however, needs further investigation, as the values of X for continuous current discharges found by different observers are not in good agreement.

With large currents the force X and the coefficient b in the above formula for E tend to diminish as the current increases. This may be attributed to the reduction of the density due to the increase of temperature of the gas, since the electromotive force E diminishes when the density is diminished (by reducing the pressure). This explanation of the changes in X and b with large currents is in agreement with the fact that the changes are much more marked in narrow tubes than in wide tubes; also the changes are augmented when the pressure of the gas is increased. The increase of temperature is proportional to the current density [$I/\pi R^2$, 2R being the diameter of the tube] and to the electric force X, which increases with the pressure.

In the experiments with large currents it is advisable to have the tubes closed so as to avoid large changes in the density due to the increase of temperature of the gas.

13. The changes in the values of X and b with the current may be seen by the curves, fig. 4, which give the values of E obtained with currents from 3 to 18 milliamperes, the wave-length of the oscillations being 40 m. These experiments were made with the secondary circuit shown in fig. 2.

The four lower curves give the values of E for the tube 3·9 cm. internal diameter containing nitrogen at ·26 mm. pressure.

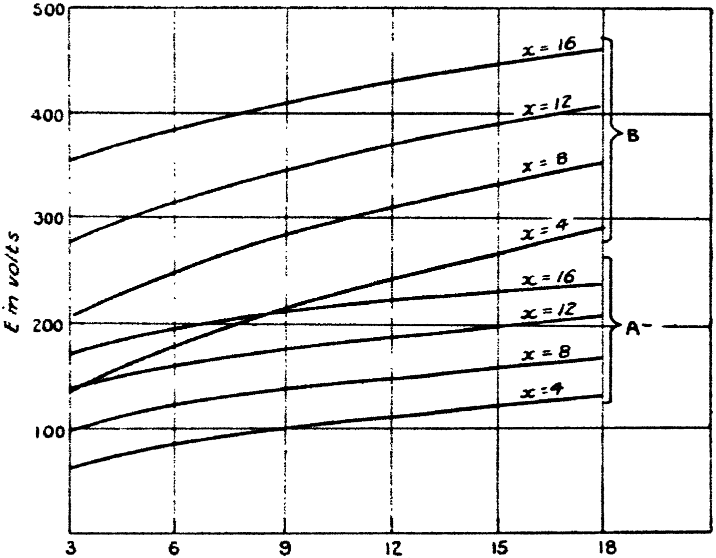
The curves correspond to the distances 4, 8, 12, and 16 cm. between the electrodes, and the value of X for any given current is $(E_1-E_2)/(x_1-x_2)$, where E_1 and E_2 are the electromotive forces for the distances x_1 and x_2 between the electrodes. In this case there is no appreciable change in X (from the value X=8·9 volts per cm.) in the b range of currents from 3 to 18 milliamp. The coefficient b, which is proportional to dE/dI, changes from the value $b=·14$ with currents from 3 to 6 milliamp. to $b=·085$ with currents from 12 to 18 milliamp.

The four upper curves (fig. 4) give the values of E for a tube 1·4 cm. internal diameter containing nitrogen at ·53 mm. pressure. In this case the force X changes with the current, the values of $(E_1-E_2)/(x_1-x_2)$ being 17·7, 16·2, and 14·8 volts per cm. for the currents 3, 9, and 15 milliamp. respectively, and the coefficient b changes from the value $b=·28$ for currents from 3 to 9 milliamp. to $b=·155$ for currents from 12 to 18 milliamp.

14. High frequency currents are maintained in helium and in neon with much smaller forces than those required to maintain similar currents in nitrogen. The electrodeless tubes used in the experiments with the monatomic gases were of quartz 30 cm. long and 4·2 cm. in diameter. With helium at 1 mm. pressure, the values of E for currents from 3 to 6 milliamp. are given by the formula :

$$E = 3{\cdot}6 \times x + {\cdot}036\,\lambda I + 16,$$

Fig. 4.



Current-electromotive-force curves, λ = 40 metres.
Curves A : nitrogen ·26 mm. pressure, tube 3·9 cm. diameter.
Curves B : nitrogen ·53 mm. pressure, tube 1·4 cm. diameter.

and with neon at 1·06 mm. pressure E is given by the formula :

$$E = 2{\cdot}5 \times x + {\cdot}035\,\lambda I + 12,$$

which show that in the helium tube the force in the uniform glow was 3·6 volts per cm., and in the neon tube 2·5 volts per cm.

Thus the electrons acquire sufficient energy to ionize atoms of the gases when moving under these forces, so that in some of the collisions with the atoms the electrons lose a large proportion of their kinetic energy.

These results are in agreement with the experiments on the motion of electrons in gases which show that with the gases at 1 mm. pressure the average loss of energy of the electrons in collisions with atoms is small with forces of the order of 1 volt per cm., but the loss increases when the force increases. This is seen by the numbers in the following table, where δ represents the fraction of the energy of an electron which is lost in a collision with an atom of the gas. The values of δ are average values when the electrons move in a uniform field. The force X is given in volts per cm., the gases being at 1 mm. pressure.

X.	·5	1.	2.	4.
Helium $\delta\times10^5$	23	24	28·5	67·5
Neon $\delta\times10^5$	7	12	49	170

15. In order to compare the potentials required to maintain discharges with external and internal electrodes, tubes were made with internal electrodes of nickel sheet in the form of sleeves, 4 cm. long which fitted tightly into the tubes. Direct connexion to the electrodes was made through wires sealed in the glass, and the electromotive force between the internal sleeves was measured in the same way as the electromotive force between external sleeves.

Tubes of the same diameter containing nitrogen at the same pressure were also made up which were used with external electrodes.

The potentials required to start the discharges were determined with tubes containing nitrogen at various pressures from ·005 mm. to 1 mm., also the minimum potentials required to maintain small currents with a uniform glow in the tubes.

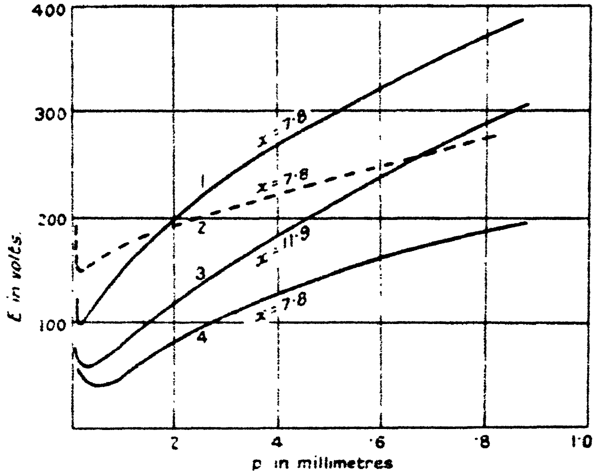
The results obtained with tubes 3·1 cm. in diameter for pressures from 0·4 mm. to 1 mm., are shown by the curves fig. 5. In this diagram the ordinates represent the potential E in volts, and the abscissæ the pressures p in millimetres, the wave-length of the oscillation being 40 m.

The potentials E required to start a discharge in a tube with external electrodes are given by curve 1 (fig. 5), and the corresponding potentials for the tube with internal electrodes are given by curve 2 (fig. 5), the electrodes being 7·8 cm. apart in each case. At pressures greater than 1·6 mm. the electromotive force between the internal electrodes is smaller, but at lower pressures it is greater than the electromotive force between external electrodes.

16. The potential required to maintain a discharge is much less than the starting potential, and there is a minimum value of the potential that maintains a current with a uniform glow in the tube both with internal and external electrodes.

In general the glow is uniform along the whole length of the tube, and the intensity of the glow increases with the amplitude of the current, but with currents below a certain value the glow disappears from a space midway between the electrodes, and the luminosity is confined to the gas near the electrodes. When the force acting on the secondary circuit is reduced (by reducing the current in the generator), there is an abrupt diminution of the current in the tube, and an increase in the electromotive force between the electrodes, when the glow disappears from the middle part of the tube.

Fig. 5.



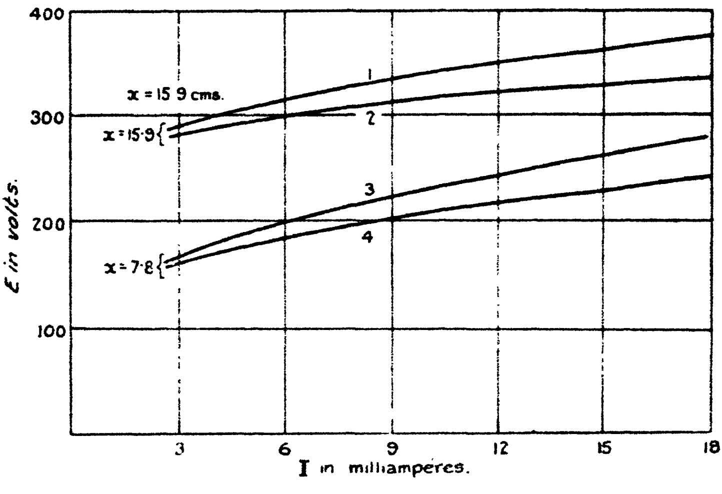
Nitrogen: tubes 3·1 cm. internal diameter, λ=40 metres.

The minimum potential required to maintain a current with a uniform glow is easily determined, as the rate of change of the potential with the current is small, when the current approaches the value at which the glow ceases to be uniform along the tube.

The minimum potentials were determined for the two tubes 3·1 cm. in diameter, one with internal electrodes and the other with external electrodes 7·8 cm. apart, also for two similar tubes with electrodes 11·9 cm. apart.

These potentials are given in terms of the pressure *p* by curves 3 and 4 (fig. 5). The minimum potentials are the same for tubes with internal and external electrodes for pressures greater than ·04 mm. At this pressure, with the electrodes 7·8 cm. apart (curve 4), the potential required to maintain a small current is 39 volts; but it increases with the pressure, the minimum potential being 81 volts when the gas is at ·2 mm. pressure and 189 volts at ·8 mm. pressure.

Fig. 6.



Nitrogen pressure ·53 mm., tubes 3·1 cm. in diameter, $\lambda = 40$.

At pressures less than ·04 mm. the minimum potential increases as the pressure is diminished, and the potential is less for the tubes with external electrodes than for those with internal electrodes. For the tubes with electrodes 7·8 cm. apart the potential was 64 volts with external electrodes and 92 volts with internal electrodes when the nitrogen was at ·01 mm. pressure.

17. The potential required to maintain large currents from 3 to 18 milliamp. were determined with the tubes 3·1 cm. in diameter containing nitrogen at ·53 mm. pressure, the wave-length of the oscillations being 40 m. The results of the experiments are given by the curves (fig. 6), where the

ordinates are the potentials in volts and the abscissæ the currents in milliamperes.

The potentials for currents in the tubes with external electrodes at distances 15·9 and 7·8 cm. apart are given by curves 1 and 3 respectively.

The corresponding potentials for currents in the tubes with internal electrodes at these distances apart are given by curves 2 and 4.

The difference between the ordinates of curves 1 and 3 is the same as the difference between the ordinates of curves 2 and 4, which shows that the force X in the uniform glow in the tubes with external electrodes is the same as the force in the tubes with internal electrodes. This force is approximately 14 volts per cm. with currents from 3 to 9 milliamp., but with larger currents the force diminishes as the current increases.

For a given current the potential E is greater with external electrodes than with internal electrodes. The difference is small, about 8 volts with a current of 3 milliamp., but it increases with the current, and with 18 milliamp. the difference is about 40 volts.

The difference between the values of E obtained with external and internal electrodes may be attributed to the fall of potential between the external electrodes and the inner surface of the tube, which is proportional to the current. Since the effect is negligible with small currents, the maintenance of the current cannot be due to any appreciable extent to electrons set free from the internal electrodes—unless electrons are set free at the same rate from the surface of the glass when external electrodes are used, which is very improbable.

18. Two tubes 3·1 cm. in diameter, with internal electrons in the form of sleeves, were used to determine the force in the positive column of a continuous current discharge in nitrogen at ·53 mm. pressure. The current was maintained by a battery of small accumulators, which was connected through a high resistance [10^5 to 3×10^5 ohms] to the electrodes, and was adjusted by changing the potential of the battery or the resistance. With this arrangement the positive column became striated with currents of the order of 1 milliamp., but with smaller currents a uniform positive column was obtained. The electrodes were 16 cm. apart in one of the tubes and 7·5 cm. apart in the other, but with the same current in each tube the difference between the lengths of the positive columns (L_1-L_2) was not 8·5 cm. (as is

usually the case with plane electrodes). With currents of 0·15, 0·2, and 0·3 milliamp. the values of (L_1-L_2) were 8·5, 8·2, and 7·7 cm., and for these currents the values of V_1-V_2 were 112, 106, and 94 volts respectively, where V_1 was the electromotive force between the electrodes 16 cm. apart and V_2 between the electrodes 7·5 cm. apart.

These numbers give the following values of the force $(V_1-V_2)/(L_1-L_2)$: 12·7, 12·9, and 12·2 volts per cm., which are the forces in the positive column. There is some uncertainty as to the accuracy of these measurements, since the values of (L_1-L_2) are not the same as the difference between the distances of a part of the electrodes in the two tubes. Further experiments are being made to check the accuracy of these determinations.

The average of the above forces, 12·6 volt per cm., may be taken as the force in the positive column of a continuous current discharge in a tube 3·1 cm. in diameter containing nitrogen at ·53 mm. pressure. The root-mean-square value of the force in a high frequency discharge in a similar tube was $X=13·7$ volts per cm., so that the average intensity of the high frequency force $(2X\sqrt{2}/\pi)$ was 12·4 volts per cm., which is in good agreement with the value obtained for the force in a continuous current.

LXXII. *On the Distribution of Charge in the Chlorine Ion in Rocksalt.* By G. W. Brindley, *Darbishire Research Fellow,* and R. G. Wood, *Manchester University*[*].

1. *Introduction.*

In comparing the quantitative measurements of the intensities of X-ray reflexions from rocksalt and sylvine[†] with theory, a fairly close agreement was obtained between the experimental F curves[‡] for Na^+, Cl^-, and $(K^+ + Cl^-)$ and the theoretical curves calculated from the radial distribution of charge in these ions, corrections being made for the thermal vibrations of the ions and for zero-point energy.

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[*] Communicated by Prof. W. L. Bragg, F.R.S.

[†] James and Firth, Proc. Roy Soc. A, vol. cxvii. p. 62 (1927); James and Brindley, Proc. Roy. Soc. A, vol. cxxi. p. 155 (1928).

[‡] F, the scattering factor for an atom, is a function of $(\sin\theta)/\lambda$ and may be defined as the ratio of the amplitude of the coherent radiation scattered from an atom in a state of rest to the amplitude scattered by a free electron according to the classical theory due to J. J. Thomson.

In each case, however, it was observed that for values of $(\sin\theta)/\lambda$ of the order of 0·4–0·5, θ being the glancing angle of incidence and λ the wave-length in Ångström units of the X-radiation, the experimental points lay markedly lower than the theoretical curves. Since the form of the F curve depends directly upon the distribution of charge in the diffracting medium, it is of interest to inquire what variations of the charge distribution will account for the discrepancy between the observed and calculated F curves.

Certain assumptions have been made in comparing theoretical and experimental F curves. Firstly, it is generally considered that in rocksalt and sylvine the diffracting centres are ions. Measurements of the intensities of X-ray spectra, while consistent with this view, do not provide conclusive proof that the atoms in these crystals are ionized. Secondly, in order to compare experimental results with theory, it was necessary to assume that the radial distribution of charge in the ions in a crystal lattice was the same as that which would exist in the ions by themselves. This cannot be more than approximately true, owing to the overlapping of neighbouring ions and their mutual interaction. A third assumption was made, namely, that the ions could be considered spherically symmetrical. Though probably true to a first approximation for the inner electrons, this will not be true for the outer ones, since these are controlled least by the parent atom and are influenced most by neighbouring atoms.

Assuming still that the atoms are ionized, the question is asked how the charge-distribution in an ion in a lattice differs from that in a free ion. The charge-distribution in a free ion is determined by the field of the ion itself, but in an ion in a lattice the distribution is modified by the field due to neighbouring ions. This modification is partly a distortion of the spherical symmetry of the free ion, and partly an alteration in the radial distribution. Reasons will be given for supposing that the departure from spherical symmetry of an ion in a lattice of the rocksalt type is probably small, so that the modification due to neighbouring ions is mainly a change in the radial distribution.

The experimental evidence so far obtained gives little information about the symmetry of ions. If they were distorted it would be expected, in general, that the values of F for spectra of different type but of the same structure factor would lie on slightly different curves. No experimental evidence of this kind has yet been obtained. This tends to show that the charge-distribution in an ion approximates to spherical symmetry, and that any departure from spherical symmetry is confined to the outer parts of the ions, the effect of which on the F curve is small. J. E. Lennard-Jones and H. J. Woods [*] have recently investigated theoretically the distribution of electrons in a two-dimensional "metal" and they find that surrounding each atom there is a circular distribution of electrons which is disturbed very little on the lines joining the centres of adjacent atoms, but that there is a certain distribution of charge in the spaces enclosed by four atoms. Such evidence as we have, therefore, tends to show that the lack of spherical symmetry is probably small, particularly for the inner "shells" of electrons.

It seems probable, therefore, that the difference between the experimental and theoretical curves may be due to the *radial* distribution of charge being altered by neighbouring ions. If we can neglect the lack of spherical symmetry, then the radial distribution of charge corresponding to the experimental F curve will be the distribution in an ion in a attice.

There is, indeed, another possibility, namely, that the approximate method by which Hartree has determined the radial distribution of charge in a free ion may not be sufficiently accurate. Reasons will be given later to show that this is probably not the case.

2. *Application of the Method of Fourier Analysis.*

A. H. Compton [†] has derived an expression by means of which the radial distribution of charge in an atom may be calculated from its F curve by a method of Fourier analysis. If $U(r)$ be the electron density at a distance r from the centre of an atom, then

$$U(r)\,dr = \frac{8\pi r}{D^2}\sum_{1}^{\infty} nF_n \sin 2\pi nr/D \,.\, dr. \quad . \quad . \quad (1)$$

In this equation, F_n is the value of F for the nth order spectrum for planes whose spacing is D. The most direct method of obtaining the radial distributions corresponding to the experimental F curves would be to apply equation (1), giving D some arbitrary value. A difficulty arises due to the factor nF_n not converging sufficiently rapidly. The experimental F curves have to be extrapolated until F is inappreciable. In practice it is found that at the greatest angles at which F_n has been measured, nF_n is still large, and a big proportion of the terms in the series $\sum_1^\infty nF_n \sin 2\pi nr/D$ depends upon extrapolated values of F, the numerical value of many of them being large. In consequence, the final result is influenced to a very large extent by the way in which the F curves are extrapolated. It is not practicable, therefore, to determine the U(r) curve by the direct application of Fourier analysis to the experimental F curve.

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[*] Proc. Roy. Soc. A, vol. cxx. p. 727 (1928).

[†] X-Rays and Electrons, p. 151 *et seq.*

The following method, which was suggested by Prof. W. L. Bragg, eliminates the difficulties arising from the direct analysis. The difference between the experimental and theoretical F curves exists only for values of $(\sin\theta)/\lambda$ of the order of 0·4 to 0·5 ; for larger values of $(\sin\theta)/\lambda$ there is a very close agreement between the curves. Since F at large values of $(\sin\theta)/\lambda$ depends almost entirely on the inner electrons, for which the distribution of charge is known with most certainty and which are influenced least by neighbouring atoms, the error incurred by assuming the two curves identical for large values of $(\sin\theta)/\lambda$ will only be small. If then the Fourier analysis be applied to the difference, ΔF, between the two curves, the series $\sum_1^\infty n\,.\,\Delta F_n \sin 2\pi nr/D$ will converge very much more quickly than the series $\sum_1^\infty n\,.\,F_n \sin 2\pi nr/D$, since ΔF_n becomes zero when F_n is still appreciable. This method eliminates the difficulties arising from the extrapolation of the experimental values of F, and the assumption which it involves is, on general grounds, justifiable.

3. *Results.*

The method has been applied to the results obtained by James and Miss Firth * for the chlorine ion, Cl^-, in rocksalt. The radial distribution of charge for this ion has been calculated by Hartree †, and the theoretical values of F for the Cl^- ion at rest are given in a joint paper by James, Waller, and Hartree ‡. In this last paper the values are also given of F for the Cl^- ion at rest, calculated from the experimental values of F at 86° Abs., by applying suitable corrections for thermal vibration and zero-point energy. The very small differences which occur between the theoretical and experimental values of F at values of $(\sin\theta)/\lambda$ greater than 1·0, which are only of the order of 0·15 of an electron, will be neglected in the present paper, since differences so small may well be due to the difficulty in measuring very weak spectra.

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* Proc Roy. Soc. A, vol. cxvii. p. 62 (1927).

† Camb. Phil. Soc. Proc. vol. xxiv. pp. 89, 111 (1928).

‡ Proc. Roy. Soc. A, vol. cxviii. p. 334 (1928).

The analysis has been carried out for two values of the arbitrary spacing D, 5 Å.U. and 10 Å.U. In Table I. values are given of F_n', calculated from the Hartree-Schrödinger radial distribution of charge and of F_n, calculated from the experimental results of James and Miss Firth, for a series of values of n, D being 10 Å.U.

TABLE I.

$D = 10{\cdot}0$ Å.U. $(\sin\theta)/\lambda = n/2D = 0{\cdot}05\,n$.

n.	$(\sin\theta)/\lambda$.	F_n' theoretical.	F_n experimental.	$F_n' - F_n$.	$n\,.\,\Delta F_n$.
1	·05	17·11	17·11	—	—
2	·10	15·23	15·23	—	—
3	·15	13·19	13·19	—	—
4	·20	11·50	11·50	—	—
5	·25	10·23	10·15	·08	·40
6	·30	9·30	9·02	·28	1·68
7	·35	8·60	8·32	·28	1·96
8	·40	8·06	7·70	·36	2·88
9	·45	7·62	7·20	·42	3·78
10	·50	7·23	6·78	·45	4·50
11	·55	6·84	6·37	·47	5·17
12	·60	6·49	6·03	·46	5·52
13	·65	6·12	5·75	·37	4·81
14	·70	5·77	5·45	·32	4·48
15	·75	5·41	5·16	·25	3·75
16	·80	5·06	4·89	·17	2·72
17	·85	4·74	4·62	·12	2·04
18	·90	4·41	4·35	·06	1·08
19	·95	4·10	4·10	—	—

In Table II. the results are given of the Fourier analyses. If $\Delta U(r)$ be the difference between the values of $U(r)$ corresponding to F_n' and F_n, then

$$\Delta U(r)dr = \frac{8\pi r}{D^2}\sum_{1}^{\infty} n\,.\,\Delta F_n \sin 2\pi nr/D\,.\,dr.$$

On the left-hand side of Table II. values are given of $\Delta U(r)$ for a series of values of r/D, the latter being chosen to facilitate the calculation of the sine terms. On the right-hand side of Table II. are tabulated values of $\Delta U(r)$ for a series of values of the radius r, these values of $\Delta U(r)$ being obtained by graphical interpolation from the results given on the left-hand side of the Table.

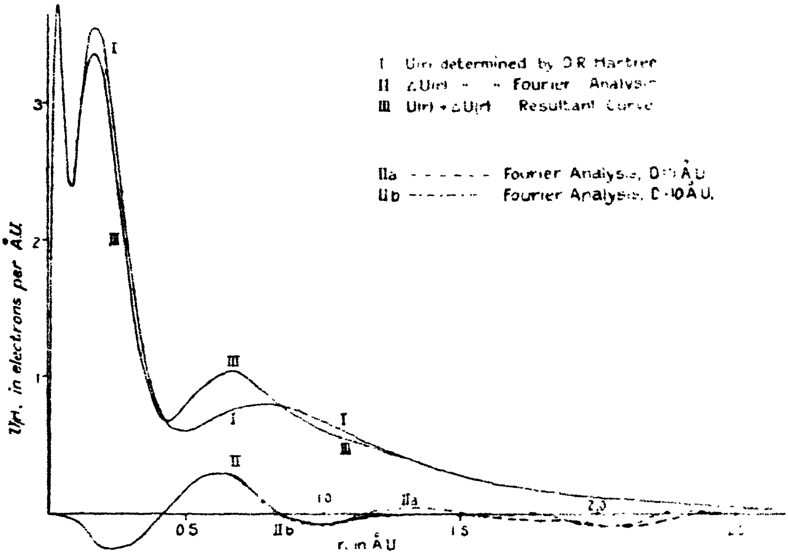
TABLE II.

r/D.	U(r) in electrons/A.U.		r in Å.U.	U(r) in electrons/A.U.	
	D=5·0 Å.U.	D=10 Å.U.		D=5·0 Å.U.	D=10 Å.U.
·025	−1·13	−2·40	0·1	−0·62	−0·56
·050	−2·45	+1·91	0·2	−2·35	−2·27
·075	−1·05	+1·34	0·3	−2·28	−2·21
·100	+1·85	−0·91	0·4	−0·47	−0·30
·125	+2·95	+0·17	0·5	+1·85	+1·91
·150	+1·51	−0·16	0·6	+2·92	+2·92
·175	−0·26	+0·01	0·7	+2·42	+2·33
·200	−0·72	−0·84	0·8	+0·60	+0·45
·225	−0·16	+0·19	0·9	−0·50	−0·60
·250	+0·36	−0·09	1·0	−0·72	−0·92
·275	+0·47	+0·55	1·1	−0·37	−0·71
·300	+0·12	+0·02	1·2	+0·21	−0·05
·325	−0·29	+1·01	1·4	+0·42	+0·20
·350	−0·51	−0·90	1·6	−0·22	−0·36
·375	−0·56	−0·59	1·8	−0·52	+0·11
·400	−0·76	−0·57	2·0	−0·78	−0·84
·425	−0·83	+0·01	2·2	−0·59	−0·37
·450	−0·38	+0·23	2·4	+0·08	+0·48
·475	+0·04	+0·81			
·500	0	0			

There is a close similarity between the two analyses for values of r less than 1·0 Å.U., but, as r increases, the discrepancy between the two analyses also increases. To some extent this is due to $\Delta U(r)$ being proportional to r. But this is not the sole cause. The arbitrary spacing D must be chosen greater than twice the radius of the atom, for when D is equal to twice the radius, the summation $\Sigma n F_n \sin 2\pi n r/D$ is zero. In taking D=5·0 Å.U., it is assumed that the charge lying outside a radius of 2·5 Å.U.

is negligible. This is only approximately true. It is probable, therefore, that the discrepancy between the two analyses is partly due to there being an appreciable amount of charge at distances from the nucleus greater than D/2. We have assumed that the oscillations of the $\Delta U(r)$ curve about the r-axis for $r > 1·0$ Å.U. arise mainly, if not entirely, from the method of analysis. From $r = 1·0$ Å.U. the $\Delta U(r)$ curve has been drawn to zero at $r = 1·5$ Å.U. in such a manner that $\int_0^\infty \Delta U(r)\, dr = 0$.

Fig. 1.



Distribution of Charge in Chlorine Ion, Cl^-.

In fig. 1, curve I is the $U(r)$ curve for the Cl^- ion calculated by Hartree. Curve II is the $\Delta U(r)$ curve which has been used to determine the $[U(r) + \Delta U(r)]$ curve—curve III in fig. 1. The actual results of the Fourier analyses, where they differ appreciably from curve II, are shown by the broken curves II *a* and II *b*, which correspond respectively with $D = 5·0$ Å.U. and $D = 10$ A.U.

The difference between the $U(r)$ curve calculated by Hartree, and the curve corresponding to the experimental F curve, is greater than can be attributed to the approximate nature of Hartree's method. Gaunt, in a recent paper[*], has discussed the validity of Hartree's assumption regarding the self-consistent field, and he shows that when small corrections are made for the spin of the electron and relativity correction, the method is legitimate. Moreover, the numerical values of the ionization potentials calculated from Hartree's constant ϵ agree closely—in some cases to within 1 per cent.—with values obtained experimentally. It seems unlikely then that the $U(r)$ curve determined by Hartree can be so much in error as the difference $\Delta U(r)$ between the two $U(r)$ curves in fig. 1.

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[*] Proc. Camb. Phil. Soc. vol. xxiv. p. 328 (1928).

It seems possible, therefore, that the difference between the theoretical and experimental values of F arises because the radial distribution of charge in a Cl^- ion in a rocksalt lattice differs from the distribution in a single Cl^- ion. If the results can be interpreted in this way, then, from fig. 1, it is seen that the maximum of the charge distribution of the M electrons in the Cl^- ion in rocksalt is sharper and occurs at a smaller radius than in the free chlorine ion.

4. *Summary.*

It has been found that the experimental and theoretical F curves for the chlorine ion, Cl^-, differ by an amount greater than can be attributed to experimental error for values of $(\sin\theta)/\lambda$ of the order of 0·4–0·5.

Reasons have been given for supposing that the lack of spherical symmetry of an ion in a lattice is small and that any departure from spherical symmetry is confined mainly to the outer part of the ion, which will have little effect on the F curve. We have therefore assumed that the difference between the experimental and theoretical F curves is due to a change in the radial distribution.

Applying the method of radial Fourier analysis to the difference ΔF between the two curves, the difference between the charge distribution in a free chlorine ion, as determined by Hartree, and in a chlorine ion in a rocksalt lattice has been calculated. Hence the charge distribution in a chlorine ion in rocksalt has been obtained.

In conclusion, we wish to thank Prof. W. L. Bragg, F.R.S., and Mr. R. W. James for suggesting this investigation and for their interest. Thanks are also due to the Department of Scientific and Industrial Research for a grant held by one of us.

Manchester University,
Dec. 19, 1928.

LXXIII. *Notes on Surface-tension.* *By* ALFRED W. PORTER, *D.Sc., F.R.S., F.Inst.P., Emeritus Professor of Physics in the University of London* [*].

I. *The Rise of Liquid in a Capillary Tube.*

THE problem of the rise of liquid in a capillary tube received its last and most complete treatment by the late Lord Rayleigh in 1915 (Proc. Roy. Soc. A, xcii. p. 184, 1915). The differential equation that must be exactly satisfied is

$$\frac{d\sin\theta}{dx}+\frac{\sin\theta}{x}=\frac{1}{\beta^2}(h+y), \quad . \quad . \quad . \quad . \quad (1)$$

where y and x are the rectangular coordinates of the meniscus reckoned from the vertex, θ the inclination to the horizontal, and

$$\beta^2 = \text{surface-tension} \div (g\times\text{density}) = \sigma/(g\rho).$$

To a first approximation (*i. e.* neglecting y) the meniscus is a circle of radius a, from which y can be calculated and inserted in the equation, and thus further approximations can be obtained.

Putting

$$y = a-(a^2-x^2)^{\frac{1}{2}}+u,$$

[or, as we may abbreviate it,

$$y=a-w+u,$$

where

$$w=(a^2-x^2)^{\frac{1}{2}},$$

whence, when needed,

$$x\,dx=-w\,dw,]$$

$$u=\left\{\mathrm{K}\frac{a^2}{w}+\frac{a^3}{3\beta^2}\log(a+w)\right.$$
$$\left.+\frac{a^5}{6\beta^4}\left[-2\log(a+w)+\frac{w}{a}-1+\frac{a}{2w}+\frac{a}{w}\log(a+w)\right]\right\}$$
$$+\text{constant of integration.} \quad . \quad . \quad . \quad . \quad (2)$$

The symbol K represents a constant obtained in the course of a previous integration.

Following the assumption which Poisson made, that u must never be allowed to attain an infinite value, the factor of the terms containing w in the denominator only must vanish, because w becomes zero when $x^2=a^2$. Hence

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[*] Communicated by the Author.

$$u=\frac{a^3}{3\beta^2}\left(1-\frac{a^2}{\beta^2}\right)\log\frac{a+w}{a}+\frac{a^5}{6\beta^4}\left[\frac{w-a}{a}+\frac{a}{w}\log(a+w)\right]$$

$$+\text{constant of integration};$$

and finally, the integration of (1) gives

$$1=\frac{ha}{2\beta^2}\left[1+\frac{a}{3h}-0\cdot1288\frac{a^2}{h^2}+0\cdot1312\frac{a^3}{h^3}\right], \quad . \quad (3)$$

as the equation by which β^2, and therefore the surface-tension, can be calculated from experimental values of h in a tube of radius a.

The object of the present note is to discuss the mode in which the constant K is determined. Poisson and Rayleigh seem to have been guided to their mode of determining it by the fact that they saw no other way. Concerning the choice of K, Rayleigh remarks, "it may appear at first sight as though we might take it almost at pleasure."

The choice actually made is somewhat arbitrary, because, whatever the fact may be, there is no *prima facie* reason for excluding all infinite values of y (*i. e.* of u). The only obvious restriction that must be attended to is that u must never attain such values as would make infinite the total weight of the liquid raised, for this must equal $2\pi\sigma.a$. Now a term in the expression for y varying inversely as w is therefore permissible, because its contribution to the total weight raised is proportional to $\int_a^0 \frac{1}{w}w\,dw$, i. e. to $\left[\sqrt{a^2-x^2}\right]_0^a$, which is finite.

In reality, we are not without a guide in the choice of the coefficient. It appears to have been overlooked completely that the value of K is *fixed* by the known curvature at the vertex. Since the total curvature there is h/β^2 and the two curvatures are equal, each of them must equal $h/2\beta^2$. The curvature can be found by twice differentiating (2), and thence it is found that, necessarily,

$$K=\frac{ha}{2\beta^2}-1+\frac{1}{6}\frac{a^2}{\beta^2}-\frac{a^4}{6\beta^4}\log 2a.$$

However, when this value is inserted in (2) it is found, finally, that *no change is required in the equation* (3) *up to the order of terms there included.*

Rayleigh's own formula for y gives the curvature at the vertex as being

$$\frac{1}{a}-\frac{a}{6\beta^2}+\frac{a^3}{6\beta^4}(\log 2-\tfrac{1}{2});$$

this can be shown from (3) to be identical with $h/(2\beta^2)$ up to the order given. Hence his assumption appears to be true in fact, although it was introduced without having any safe basis.

The question whether infinite values of y are permissible or not can be discussed on other lines. At the vertex (equation (1)) the two curvatures are equal, and equal to $h/(2\beta^2)$. At the tube wall, the second curvature is $1/a$; so that, if Y is the value of y there, the first curvature becomes

$$C_1=\frac{1}{\beta^2}(h+Y)-\frac{1}{a}.$$

To require an infinite value of Y would require, therefore, an infinite curvature at the wall. These demands would appear to be incompatible for the kind of curve with which we have to deal.

II. *The Weight of Drops from Tubes of Various Diameters.*

This question has also been discussed by Lord Rayleigh (Phil. Mag. xlviii. pp. 321–337, 1899), and he deduces the dimensional equation

$$M=\frac{\sigma d}{g}f\left(\frac{\sigma}{g\rho d^2}\right).$$

On testing this equation by experiment, he finds that wide ranges of the term in the brackets give fairly constant values for $Mg/(\sigma d)$. Since we have no reason to expect that the diameter, D, of the drops bears a constant ratio to the diameter, d, of the tube, a function of a/D will also enter into the equation. The character of the experimental results obtained can be best understood if the variable in the brackets is changed by multiplying it by the zero-dimensional quantity $Mg/(\sigma d)$ or $\rho D^3 g/(\sigma d)$. Including both of these changes,

$$Mg/(\sigma d)=f\left[\frac{\sigma}{g\rho d^2}\cdot\frac{\rho D^3 g}{\sigma d},\ \frac{d}{D}\right]$$
$$=\phi\left[\frac{d}{D}\right],$$

so that everything disappears on the right hand except a function of the ratio of the characteristic dimensions of tube and drop. Experiment shows that the left hand has a minimum value for a particular external diameter of the tube; hence no simple-power law for the function ϕ will suit.

Treating the problem as a static one, the above seems to give all that can be obtained by this method. Since the problem in the case of falling drops is partly a kinetic one, the question of viscosity arises. Determining in the usual way suitable numerics as independent variables, the equation becomes

$$\frac{\mathrm{M}g}{\sigma d} = f_2\left[\frac{g\rho^2 d^3}{\mu^2},\ \frac{d}{\mathrm{D}}\right].$$

Now, for a given tube the weight of a drop of olive oil is not conspicuously different from that of a water one, although its kinematic viscosity (μ/ρ) is a hundred times as great. We may therefore conclude that the viscosity has very little influence in practice.

III. *The Vanishing of Surface-tension near the Critical Point.*

Professor Callendar's recent experiments on steam (Proc. Roy. Soc. A, Sept. 1928) appear to show that the meniscus between the liquid and gaseous phases of steam disappears some six degrees below the critical point, the two temperatures being about 374° C. and 380° C. respectively. At the temperature of vanishing there is a difference of density (ρ steam $=0{\cdot}6\ \rho$ water). Measurements have been made for water to nearly 380° C.: it was not found possible to make similar measurements for steam beyond 374° C., but the part of the curve obtained extrapolates without difficulty to meet the liquid curve in the neighbourhood of 380° C.

In the theory of capillarity, as worked out by Laplace, vanishing of the surface-tension should take place only when the densities of the two phases are the same. The object of this note is to point out that this is found not to be so when an attempt is made to get a better approximation by recognizing that the centres of molecules cannot approach nearer than their diameter. Laplace took the whole substance as a continuum, and certain of his integrations are effected between zero and infinity instead of between a distance comparable with the molecular diameter (s) and infinity. The Dutch school has made the change (which is by no means a slight one, because the range from 0 to s is infinitely important compared with the remainder for forces taken as varying as an inverse high power of the distance between centres).

Assuming the inverse *n*th power of force between molecules, the surface-tension is $\rho^2 F$, where F is a function which might plausibly be the same even for different kinds of matter; but on the modified theory F may be written $\frac{f}{s^{n-5}}$ where *n* is the inverse-power law of force and the surface-tension between any two media becomes

$$\sigma_{12} = \rho_1^2 F_1 + \rho_2^2 F_2 - 2\rho_1\rho_2 F_{12},$$

where

$$F_1 = f/s_1^{n-5}, \quad F_2 = f/s_2^{n-5}, \quad F_{12} = f/s_{12}^{n-5}.$$

On Laplace's theory, where the values of F are all the same,

$$\sigma_{12} = (\rho_1 - \rho_2)^2 F,$$

so that the tension vanishes only when the densities ρ_1 and ρ_2 are equal. Another possibility arises in the more general case. To take as simple an illustration as possible, let us assume that $n = 7$, and that s_{12} can be taken as the geometric mean of s_1 and s_2; then

$$\sigma_{12} = f\left\{\frac{\rho_2}{s_2} - \frac{\rho_2}{s_1}\right\}^2,$$

and it appears that

(1) if the molecules are alike when the densities are alike, σ_{12} then equals zero;

(2) the relative tension will also be zero if $\frac{\rho_1}{s_1} = \frac{\rho_2}{s_2}$.

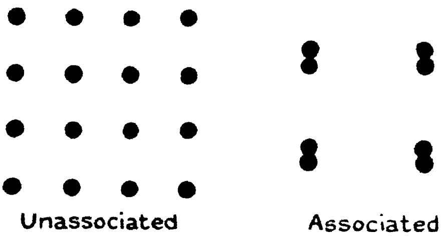
For example, let us suppose as for steam that $\rho_2 = \cdot 6\,\rho_1$, then at that point the surface-tension is zero (and the meniscus becomes plane), provided that $s_2 = \cdot 6\,s_1$. Such a possibility may easily arise if the vapour associates on condensing into a liquid, as the following diagram shows (fig. 1):

Here, in the second phase the density is greater, and yet the distance between neighbouring molecules is also greater. If the temperature is increased until the mean distances happen to be in the right proportion, the surface-tension vanishes, in spite of the inequality in the densities. Moreover, if at some higher temperature the liquid dissociates so that the molecules become of the same complexity as in the vapour state, the surface-tension will again vanish when the densities become equal.

The curve of surface-tension against temperature will in such cases become somewhat as shown in fig. 2.

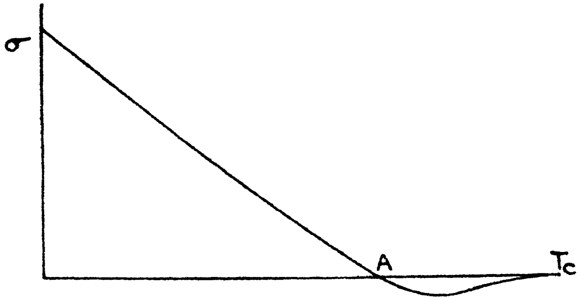
This result is in accordance with the measurements of the latent heat of steam; it is at the higher of these two temperatures that the latent heat vanishes. Now E. T. Whittaker has shown that there is a close parallelism between the *internal* latent heat and the surface energy, u. Thermodynamically the connexion between u and σ is

Fig. 1.



$$u = \sigma - T\frac{\partial\sigma}{\partial T}.$$

Fig. 2.



Since u may be expected to vanish when L_{int} vanishes (*i. e.* at T_c), then $\frac{d\sigma}{dT} = 0$ at that point. At the lower point, A, σ vanishes, but L_{int}, and therefore u, do not vanish. This indicates that at A, $d\sigma/dT$ is not zero. The diagram shows that it has a negative value there, and therefore u is positive as we would expect.

When the problem is studied from the point of view of Eötvös's law, it is recognized that his straight line extrapolated does not pass through the critical point, but some 5 to 7 degrees below it. This fact is usually accommodated to thermodynamical requirements by representing the surface-tension by an equation such as $\sigma = A(T_c - T)^n$, where n is about 1·2. But in view of the considerations brought forward in this note, the question arises whether, after all, a curve such as is shown in fig. 2 represents in reality a usual instead of an exceptional case. It must be mentioned that the case of steam is not the only one that shows the two special temperatures. Even Waterston, making experiments in closed tubes after the manner of Cagniard de la Tour, found that the cup-shaped meniscus caused by capillarity ceased at a temperature considerably under the point of transition (Phil. Mag. Jan. 1858). In alcohol the surface became quite flat at 422° F., while the transition occurred at 540° F. The relative densities of vapour and liquid at the lower point were 0·222 and 0·480. He quotes Wolf (*Ann. de Chimie*, xlix.) as showing that for ether the temperatures are 190° C. and 200° C. Both Wolf and Waterston observed a *convexity* of the surface between these temperatures. This, of course, does not mean that the interfacial tension becomes negative, but it is consistent with such a value.

It is not to be supposed that the suggestion made here is sufficient to account for the whole of the quantitative behaviour of steam in contact with water. If there are indeed two or more types of molecules present (associated and dissociated), we have to deal with at least a binary mixture, and any of the complications investigated by van der Waals, Kuenen, Roozeboom, Verschaffelt ($H_2 + CO_2$), Caubet ($CO_2 + SO_2$), Smits (anthrachinone and ether), and others may arise. The theory has only been worked out for binary mixtures of distinct components. In the case of steam, according to Callendar we are dealing with two states of the same component, *i. e.* a mixture in which the two types of molecule can transform into one another. I am not aware that the case of a dissociating mixture has yet been dealt with theoretically. One would anticipate it to be a problem of extraordinary difficulty.

87 Parliament Hill Mansions, N.W. 5.
January 25, 1929.

LXXIV. *On the Separation of Isotopes.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

WE should be glad if you would allow us to make a short comment on the paper of Harkins and Mortimer published in the October issue of the Philosophical Magazine. This paper deals with the problem of the Separation of Isotopes, and contains also a detailed account of the history of the subject. Early attempts were made to separate the radioactive isotopes by diffusion in liquids, and especially to separate uranium 1 from uranium 2; but these attempts failed. To explain this failure, it was pointed out that the rate of diffusion of ions in liquids is practically independent of the mass, and is inversely proportional to the radius; as the radius of the isotopes is practically identical, hardly any separation could be expected by this method. Even at this early date it was suggested that in a gaseous medium diffusion is bound to lead to a separation of isotopes. Such an attempt was, in fact, made by Aston quite independently of the above considerations. As announced at the meeting of the British Association at Birmingham in 1913, he was successful in obtaining a partial separation of the isotopes of neon by diffusion.

In 1920 the present writers attempted the separation of the isotopes of mercury; they based their method on an entirely new principle—namely, that the rate of evaporation of isotopes must be inversely proportional to the square root of their atomic weights. This method allows an exact calculation of the effect to be expected, and in our experiments we obtained a long series of results which were in the best agreement with the theoretical values. The partial separation of the isotopes was followed by density measurements, and the reality of the phenomenon was proved by the fact that the various samples retained their density values unchanged on ordinary distillation. Furthermore, a measurement of the electrical conductivity of the fractions obtained was carried out by Jaeger and Steinwehr, who found the conductivity of the various samples to be identical within about one part in a million, and from this it was concluded that no impurities were present. Finally, Hönigschmid determined the atomic weight of the fractions obtained, and found that these agreed well with the values calculated from density differences.

In view of these facts, we have some difficulty in understanding the remarks of Harkins and Mortimer, in the paper quoted above, that we gave no evidence that our mercury was pure.

Aston's diffusion method and our method of ideal distillation were used by Harkins and his collaborators §, by Egerton, and by others. By improving the technique of the experiments and by laborious work, Harkins and Mortimer succeeded in obtaining mercury fractions the atomic weight of which differed by 0·2 of a unit. The present writers seven years ago obtained mercury fractions the atomic weight of which differed by 0·1 unit. This illustrates clearly the fact that, while methods based on the difference of molecular velocities are very useful in obtaining a partial separation, they are quite incapable of effecting a full separation.

Yours faithfully,
J. N. Brönsted and G. Hevesy.

LXXV. *The Corona Discharge in Neon.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In the April issue of the Phil. Mag. (vol. v. No. 30, p. 721) Mr. Huxley published an article on the corona discharge in helium and neon. He found that, at higher pressures, the negative discharge (wire cathode) started at a higher potential difference than the positive; this effect was especially very pronounced in neon. In the opinion of Mr. Huxley this result forms a strong argument against the theory that in corona discharges the electrons should be liberated mainly from the cathode by the action of the positive ions.

When this article was published, I had done some work on sparking potentials between coaxial cylinders in argon and neon. These experiments showed that the effect mentioned previously manifested itself only in case the gas was not quite pure. In order to perform measurements directly comparable with those of Mr. Huxley, a tube was designed with an electrode system of about the same dimensions, but of a more simple construction. The outer cylinder was made of chromium iron (diameter 4·6 cm.) which was sealed to the glass; the inner cylinder consisted of a nickel wire (diameter 0·175 cm.) protected on both sides by glass insulation. In a side-tube another electrode system was mounted in order to determine also the sparking potential between parallel plates (distance about 1 cm.) for the same gas. After pumping the whole apparatus at high temperature in the usual way, 40 mm. neon gas was admitted, which then was freed from traces of impurities by a glow discharge. From little side-tubes small amounts of argon could be admitted.

The results for the starting potentials of the positive, the negative discharge, and the discharge between the parallel plates are given in the following table:—

Gas.	Wire positive.	Wire neg.	Parallel pl.
Neon..................................	616 V.	555 V.	512 V.
Neon + 0·0001 per cent. Ar ...	490 V.	542 V.	477 V.
Neon + 0·0004 per cent. Ar ...	309 V.	465 V.	408 V.
Neon + 0·0011 per cent. Ar ...	208 V.	400 V.	334 V.

Now, it was shown previously (F. M. Penning, *Naturwissensch.* xv. p. 818, 1927; *Zs. f. Phys.* xlvi. p. 335, 1928; *Physica*, viii. p. 13, 1928; *Versl. Kon. Ak. v. Wet. Amsterdam*, xxxvii. p. 308, 1928) that the effect of very small traces of impurities on the sparking potential of neon is brought about by the circumstance that the impurities are ionized by excited (and especially by metastable) neon atoms. As the laws for the generation etc. of these metastable atoms may be different for the positive and negative discharge, there may be also a large difference in the sparking potentials in these two cases. At any rate, according to the present experiments the effect to which Mr. Huxley refers does not exist in pure neon; the starting potential is there even somewhat higher for the positive discharge than for the negative. So the experiments of Mr. Huxley give no material against the theory that electrons should be set free from the cathode by the action of the positive ions.

Yours faithfully,
F. M. Penning.

Natuurkundig Laboratorium der
N. V. Philips' Gloeilampenfabrieken,
Eindhoven (Holland).
December 1928.

LXXVI. *Notices respecting New Books.*

The Evolution of the Igneous Rocks. By N. L. BOWEN. (Princeton University Press. 1928. Price $5.00.)

THIS book embodies a course of lectures delivered to advanced students, and—as defined in the preface—is designed to interpret the outstanding facts of igneous-rock series as the result of fractional crystallization. The use of the term "evolution" is intended to designate a process of derivation of rocks from a common source.

The subject of fractional crystallization is taken up in the sixth chapter. We find, as we expect, that the mother substance is essentially basalt. Later, Professor Bowen defines such mother substances as not far from saturation with pyroxene and plagioclase, and he refers to the Deccan traps and plateau basalts in general as representing the parent magma. In this he is in accord with other writers—notably Daly. Here, also, he defines the ophitic structure of basalts as probably due to simultaneous formation of two minerals, one of which (the felspar) possesses the greater tendency towards idiomorphism. This important subject is developed with the same clearness and attention to detail which characterizes this book.

Further on Professor Bowen expresses his adherence to Daly's view that basaltic magma acts as heat-bringer, and enters into igneous rock economy on a different basis from all other magmas—a thesis fully developed by Daly in his 'Igneous Rocks and their Origin,' who claims that the facts of volcanic geology seem to cooperate with the facts of plutonic geology in showing that the essential process in igneous action on our planet is the rise of basaltic magma from the universal substratum along abyssal fissures.

Such great generalizations clearly define the importance of petrological science as contributory to our knowledge of the surface history of the earth. Professor Bowen himself has done much to advance views as to the fundamental character of basaltic magma. The view that anorthosites and peridotites arise out of crystal accumulations in basaltic magma is now generally accepted. Evidence that these important rock-materials were ever in the liquid form has not been forthcoming. This important generalization is largely referable to the earlier work of Professor Bowen.

On the subject of the origin of many granitic magmas little is as yet known. The primitive origin of granite on a great scale as contributing to the earth's acid shell is generally, of necessity, accepted.

Professor Bowen refers to the question of the melting points of basalt and of granite. Doubtless both time-element and dynamic-element enter into this difficult question. The present writer, with a view to bringing in the time-element, made experiments many years ago on rock-forming minerals, an account of which appears in the *Compte-rendu* of the International Geological Congress of 1900. They are, on the whole, opposed to the recent results of Shepherd and Craig, to which he refers. And, on the large scale, the present writer has not arrived at their result. A cube of fine-grained granite, floated for some hours in fluid basalt, when ultimately sectioned showed its external form to be unaltered; the quartz still vigorously double-refractive—the felspar more or less vitrified; the muscovite altered to the extent of liberation of its water of crystallization; the biotite slagged. Moreover, fluid basalt may be retained in a silica crucible for an indefinite time without any apparent effect upon the crucible. The data cited by Clarke in his 'Data of Geochemistry,' 5th edition, are to the same effect.

Passing over many matters of interest, we arrive at a concluding chapter on "Petrogenesis and the Physics of the Earth," which is more comprehensive than any statement upon this subject offered by American or British petrologists within recent years, so far as the present writer is aware.

Professor Bowen considers that geologic evidence respecting the outer layers of the earth favours the larger estimates arising out of seismic observations, *i. e.* a granitic layer about 25 kms. in thickness, gradually changing through intermediate to basic rocks, which give place abruptly to an ultrabasic layer at a depth of about 60 kms. [Recently Conrad has shown that the thickness of the granitic layer appears to be about 40 kms. (*Gerlands Beiträge zur Geophysik*, xx. p. 275).]

Professor Bowen objects decisively to the assumption that below a certain level (10 to 20 kms. of average granite) there must be no radioactive substances, or that their quantity must fall off so rapidly as to become negligible. "This result is not acceptable. Below the granite layer there must, in any rational scheme of things, be intermediate and basic rocks whose radioactive content is far from negligible. Below these again the ultrabasic rocks must be regarded as having the lower, but still important, quantity of radioactive substances usually found in ultrabasic rocks." He refers to certain of the earlier objections which have been raised to the view that thermal cycles are responsible for the discharge of deep-seated accumulation of heat, but adds: "In spite of the various objections, it is not improbable that an hypothesis involving periodic discharge of heat in great quantity will ultimately be preferred."

Finally he discusses the nature of the deep-seated ultrabasic layer, favouring, on the whole, the view that it is peridotic in character, but admitting the possibility that it may be eclogite, as suggested by Holmes and the present writer.

It is impossible, in the available space, to do adequate justice to Professor Bowen's comprehensive book. It is lucidly written and illustrated with many excellent diagrams. It will be valuable to the advanced student, and will certainly find a place in the library of all who are interested in the science of the rocks or in geophysics generally. J. J.

Annual Tables of Constants and Numerical Data.—Chemical, Physical, Biological, and Technological. Vol. VI. (1923–24). [Part I., pp. xxxiv+680; Part II., pp. xxix+995.] (Paris: Gauthier-Villars et Cie. 1927–28. Price: paper covers, 530 f.; bound, 610 f.)

These volumes are the latest additions to the well-known series of Annual Tables of Constants and Numerical Data, which are published under the patronage of the Union of Pure and Applied Chemistry by an International Publishing Committee, subsidised by numerous governments, academies, scientific societies, industrial societies, commercial firms, and private individuals. They contain all the numerical data that have appeared in the scientific publications throughout the whole world for the years 1923–24.

As compared with previous volumes, several additions and improvements have been made. The additions include chapters on Photography, Radioelectricity, and Geophysics. In the chapter on Engineering and Metallurgy the whole of the text is given in both French and English, and it is intended that this improvement will be made throughout the whole of succeeding volumes. Another improvement is the addition of detailed indexes to several of the chapters.

Volume VII., covering the years 1925–26, will be published during the present year.

Certain of the chapters, such as Spectroscopy, Photography, Radio-electricity, Electricity, etc., are published separately, which is a convenience for those who do not require the whole volume. Specimen pages of these and any further information can be obtained from M. Ch. Marie, General Secretary of the International Publishing Committee, 9 rue de Bagneaux, Paris (VI.).

The Principles of Thermodynamics. By G. Birtwistle. Second Edition. [Pp. ix+168.] (Cambridge: At the University Press. 1927. Price 7*s.* 6*d.* net.)

The second edition of Mr. Birtwistle's small volume on the Principles of Thermodynamics is essentially the same as the first edition, with the exception that a chapter on Nernst's heat theorem has been added. Minor revisions have also been made where required. That so few changes have been found necessary for the second edition indicates that the concise, well-balanced treatment of the subject is well adapted to the needs of the student who is desirous of obtaining a logical understanding of the principles of thermodynamics. The volume can be strongly recommended as a concise introduction to the subject.

Lehrbuch der Physikalischen Chemie, von Dr. Karl Jellinek. Fünf Bände. II. Bd. Bogen 1–17. [Pp. 272 mit 241 Figuren.] (Stuttgart: Ferdinand Enke, 1928. Preis M.21; geheftet.)

The first volume of the new edition of Dr. Jellinek's 'Lehrbuch' was reviewed recently in these pages. Each of the remaining volumes will be issued in three sections, at intervals, at the rate of one volume per year during the years 1928 to 1931. The first section of the second volume has already appeared: it deals with the properties of matter in the solid state, both isotropic and anistropic bodies being considered. A large portion is devoted to the crystalline state, the classification of crystals, crystal properties, axes, angles and planes of symmetry, including an account of the information derived from the diffaction of X-rays by crystals.

The elastic and thermal properties of solid bodies are considered in detail, including sections on specific heat, calorimetry, thermal conductivity, melting and solidification, and the effect of pressure on melting point, sublimation and the quantum theory of specific heats.

Theoretical consideratiohs are throughout carefully explained and experimental methods are considered in great detail. Numerous tables of observational data increase the value of the work for reference purposes. The volume is one which should find a place in every chemical or physical library.

Lehrbuch der Physikalischen Chemie, von Dr. Karl Jellinek. Zweite Ausgabe. Bd. II., Bogen 18–35. [Pp. 273–560; Preis M.24]; Bd. II., Bogen 36–58 u. Titelbogen. [Pp. 561–924+xv; Preis M.32]. Bd. II., Vollständig. [Pp. xv+924. mit 384 Figuren und 148 Tabellen. Preis: geh. M.88; geb. M.92.] (Stuttgart: Ferdinand Enke. 1928.)

The two sections of Bd. II. of Jellinek's 'Lehrbuch' complete the second volume. The remaining three volumes will be published in the years 1929, 1930, and 1931 respectively. The parts under review deal first with the application of kinetic and thermodynamical considerations to specific heat, entropy, melting and solidification, heat conductivity, surface energy of crystals, &c. The properties of gaseous and fluid mixtures are then considered, including diffusion of gases, osmotic pressure and its measurement, boiling and freezing points, &c. The final section deals with crystalline mixtures.

Both theoretical and practical aspects of the subjects dealt with are treated very fully. The mathematical factors are clearly expounded and can be followed without difficulty by those with but an elementary knowledge of mathematics. The text is illustrated by numerous figures and tables of numerical and experimental data. On account of its completeness and the care exercised in its compilation, the volume will serve not only as a text-book but also as a valuable work of reference.

Statistical Methods for Research Workers. By R. A. Fisher, Sc.D. (*Biological Monographs and Manuals*, No. V.) Second Edition. Pp. xiii+269. (Edinburgh: Oliver & Boyd, 1928. Price 15*s*. net.)

The appearance of a second edition of this work at an interval of three years after the publication of the first edition is an indication that it has met the needs of those who, in the course of research work, have to analyse large masses of data by statistical methods. The success of the work is doubtless due in large measure to the fact that it deals with what the statistical worker wants—"methods" and excludes proofs which in general involve the use of mathematics and of logical reasoning far beyond the average equipment of such workers. Those who require to study the proofs of the methods outlined in the book may find them in original papers or other publications, a detailed list of which is given.

The methods outlined in the book are illustrated by a large number of examples which serve to make clear the manner in which the methods are used. A series of tables given in the course of the text are reprinted on folders at the end, and can be cut out and suitably mounted for practical use.

The first edition has been revised and some additions made. The most important of these is a new chapter dealing with the principles of statistical estimation. The table of z has been considerably enlarged.

The volume forms one of a series of Biological Monographs, and has been written primarily with a view to biological workers. The subjects dealt with include tests of goodness of fit, independence and homogeneity; tests of significance of means, difference of means; regression and correlation coefficients; interclass and intraclass correlations; and the analysis of variance. All those who are concerned with such subjects will find the volume to be of great assistance to them.

Handbuch der Experimentalphysik. *Herausgegeben* von W. Wien und F. Harms. Bd. xviii. *Wellenoptik und Polarisation, bearbeitet* von K. F. Bottlinger, R. Ladenburg, M. v. Laue, Hans Schulz. *Photochemie*, von E. Warburg. [Pp. xiv+674, with 271 figures.] (Leipzig: Akademische Verlagsgesellschaft, m.b.H. 1928. Preis: brosch. 61,80; geb. 63,50 M.)

The new volume of the comprehensive treatise on experimental physics, edited by Profs. Wien and Harms, is devoted mainly to undulatory optics and the phenomena of the polarization of light. It includes sections on:—(1) The determination of the velocity of light in bodies at rest, by Prof. Ladenburg; (2) The optics of moving bodies, by Prof. v. Laue; (3) The relativity red displacement of special lines and gravitational deflexion of light, by Prof. Bottlinger; (4) The reflexion and refraction of light at the boundary between two isotropic media, by Prof. v. Laue; (5) The interference and diffraction of electromagnetic waves (excluding Röntgen rays), by Prof. v. Laue; (6) The polarization of light, including crystal optics, by Prof. Schulz. The volume is completed by a monograph on photochemistry by Prof. Warburg; the original intention had been to include this in one volume with electrochemistry, but the delay in completion of the section devoted to the latter has necessitated a rearrangement.

Special emphasis is necessarily laid throughout on experimental methods and results. The theoretical aspect is nevertheless not overlooked, and receives adequate treatment. The volume is fully up to date, *e.g.* an account is given of Michelson's recent redetermination of the velocity of light. In an encyclopædic work of this nature, limitations of space hardly enter into consideration, and, with the exception of the relativity displacements of spectral lines and deflexion of light, each subject is dealt with in a comprehensive manner. The sections dealing with the velocity of light and with optical phenomena in moving bodies summarize all that has been done on these subjects. The sections dealing with interference, diffraction, and polarization are excellent, and contain a vast amount of information. Full references to original authorities are given throughout.

The printing and general production are of good quality, but the price, as in the case of most recent German publications, is high.

Chemical Encyclopædia. By C. T. KINGZETT, F.I.C., F.C.S. Fourth Edition. [Pp. viii.+807.] (London: Baillière, Tindall, & Cox. 1928. Price 35*s.* net.)

KINGZETT's Chemical Encyclopædia is well known as a valuable work of reference for professional chemists, chemical engineers. manufacturers, students, etc. The whole of the material in the previous edition has been revised for the new issue, and extensive additions have been made, so that the new edition contains 200 more pages than the last. A valuable new feature is the inclusion of numerous bibliographical references, indicating where further details on any particular subject may be found. The usefulness of the work has thereby been greatly increased.

The subject-matter, as summarized by the compiler, comprises " pure, physical, and applied chemistry; descriptions of the elements and their chief compounds (organic and inorganic), as also the methods of their preparation, characters, and uses; brief accounts of ores and other natural products, together with their utilization; and the more important chemical terms and theories. In particular, increased attention has been given to chemical industries and the applications of chemistry in trades, the arts, and manufactures generally." There is no other work giving such varied information in a single volume; the references are remarkably complete and accurate. The author is to be congratulated on this new edition.

Magnetic Properties of Matter. By KOTARO HONDA, D.Sc. [Pp. ix+256, with 213 figures.] (Tokyo: Syokwabo & Co. 1928. N. p.)

THE original Japanese edition of this work was published in 1917. The English translation (by the author himself) will make available to a wider circle of readers a volume which is particularly valuable for the account of experimental work on the subject of the magnetic properties of matter. In this field of research Japanese investigators have taken a prominent place, and the original publications are not always easily accessible.

The volume has been enlarged and revised where necessary in translation in order to take account of progress in the science of magnetism since the original Japanese edition. The chapter dealing with theories of magnetism has been rewritten and the additions include a chapter on the magnetic moment of atoms. The volume therefore contains a well-balanced account of the present state of observation and theory. The publishers deserve to be congratulated upon the excellence of the printing and general appearance of the volume.

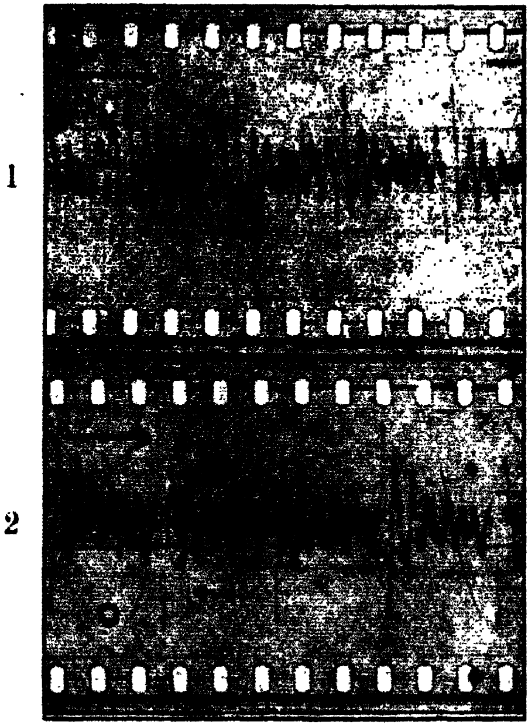
Collected Researches, National Physical Laboratory. Vol. XX, 1927. [Pp. v+444.] (London: H.M. Stationery Office. 1928. Price 18*s*. 6*d*. net.)

THE latest volume of collected researches of the National Physical Laboratory contains reprints of papers by various members of the staff, the originals of which were published between 1920 and 1927 in various scientific publications. It is devoted mainly to geometrical optics, colorimetry, and photometry. Nearly one-half of the volume contains papers on various optical problems by Mr. T. Smith. Amongst the other contents may be noted papers dealing with the colour temperature and luminous efficiency relation for tungsten, with the performance and design of the optical system of ships' navigation lanterns and with methods of measurement by optical projection.

All the volumes of the 'Collected Researches,' with the exception of Volume I., which is now out of print, can be obtained from H.M. Stationery Office, Adastral House, Kingsway, W.C. 2. They form a valuable record of much of the important work carried on at the great Institution from which they emanate.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

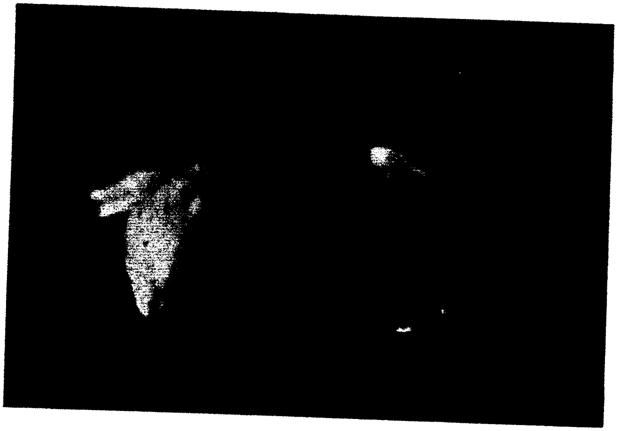
FIG. 11.



Vowel ā: film 2 taken normally; film 1 taken with phases of components shifted.

There is no difference audible between 1 and 2.

FIG. 1.



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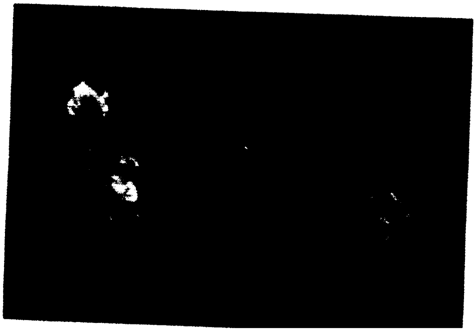


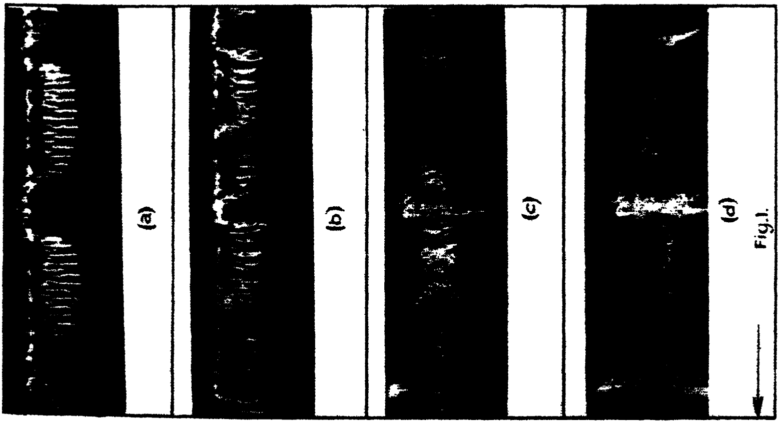


Fig. 1.

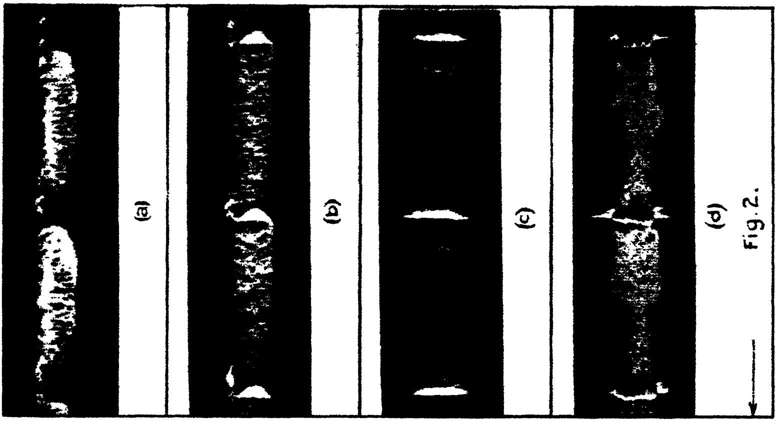
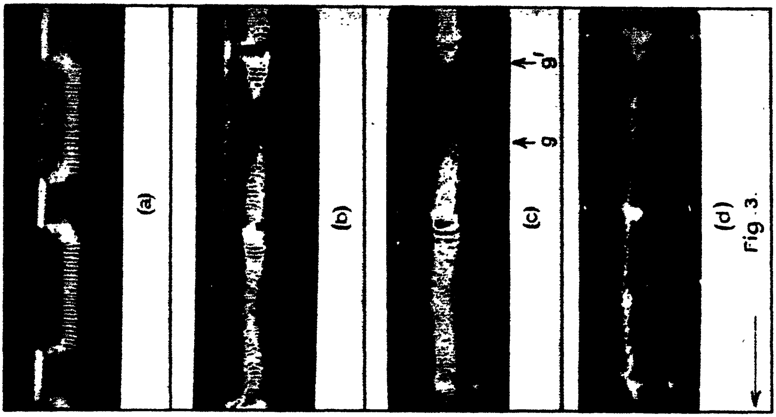


Fig. 2.



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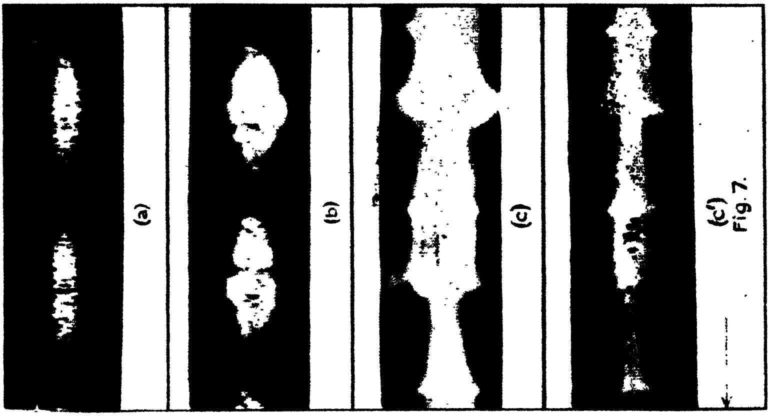

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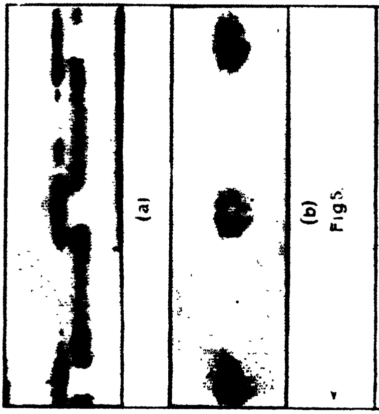


Fig. 5.

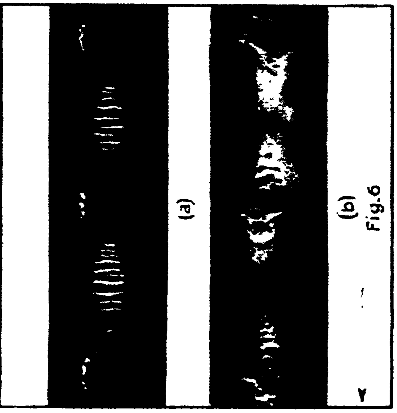


Fig. 6.

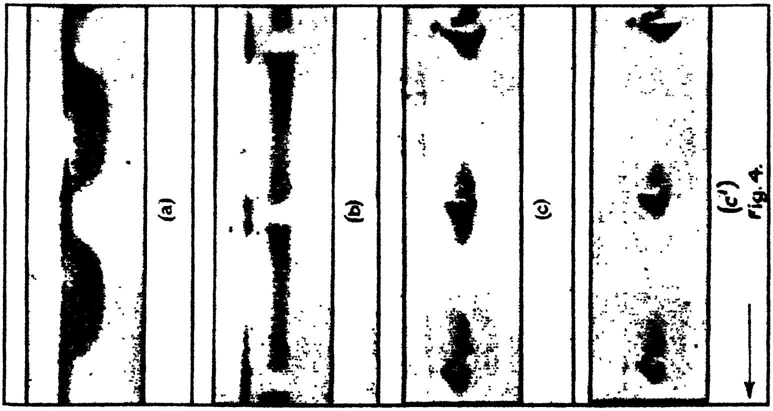
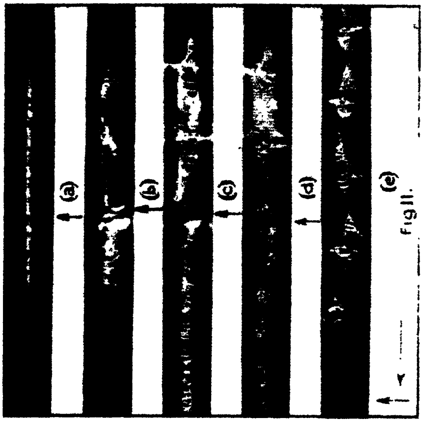


Fig. 4.



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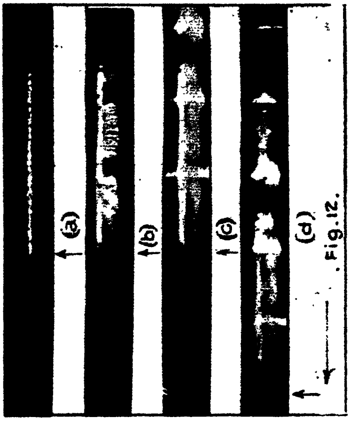


Fig. 12.

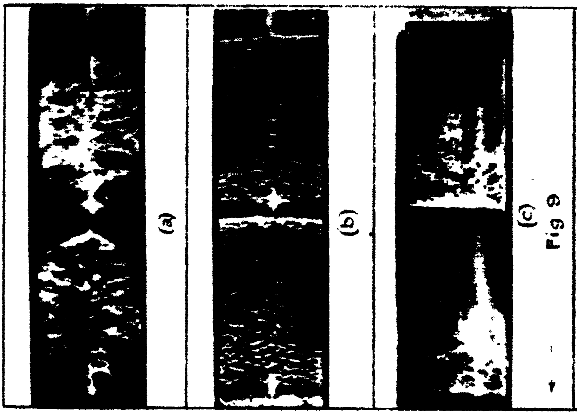


Fig 9

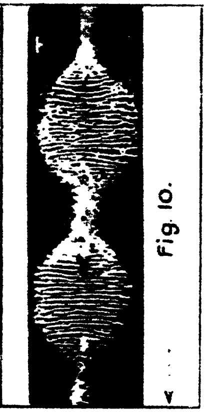


Fig. 10.

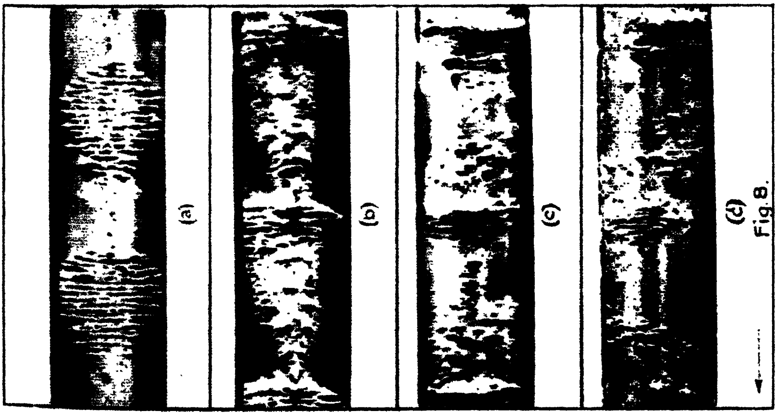


Fig. 8.

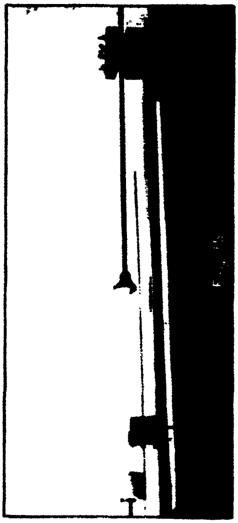


Fig. 15.

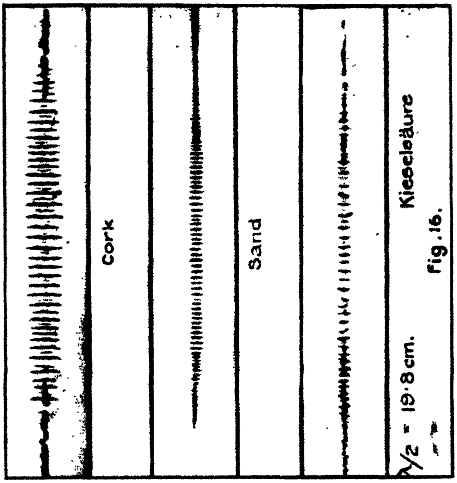


Fig. 16.

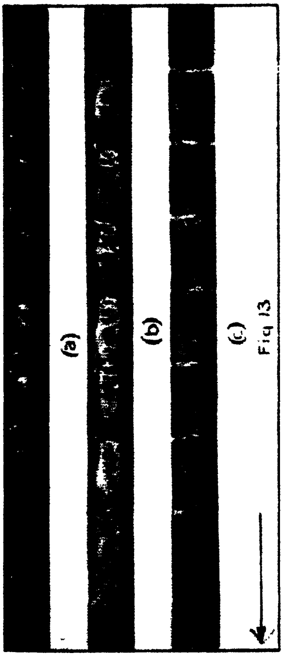


Fig 13

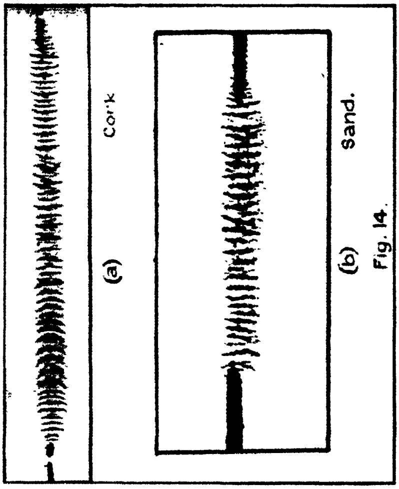


Fig. 14.

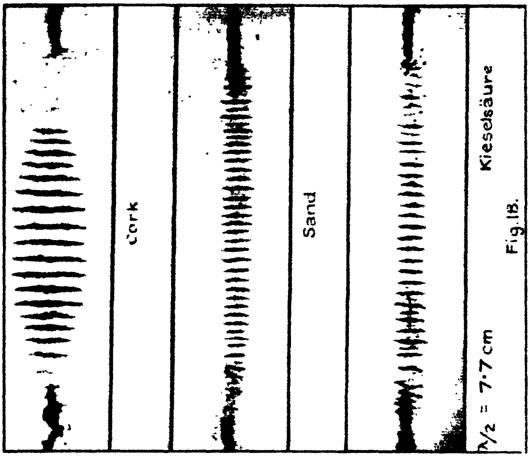


Fig. 18.

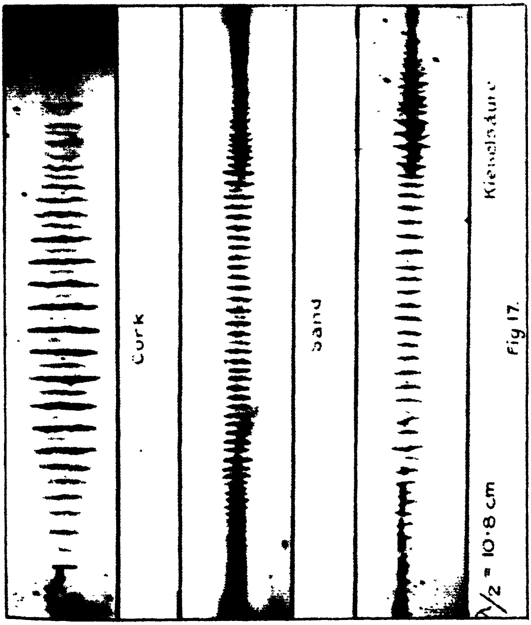


Fig. 17.

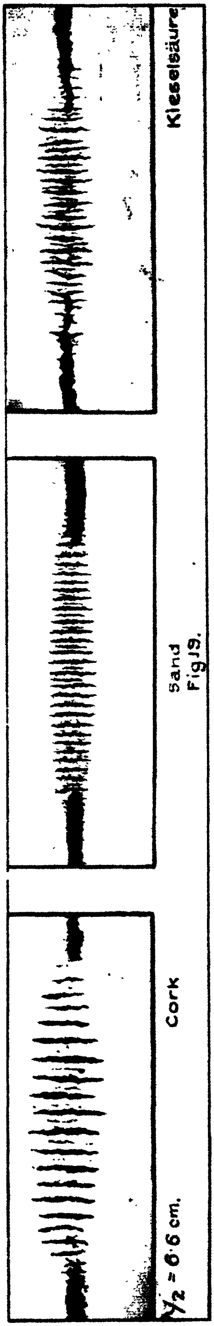
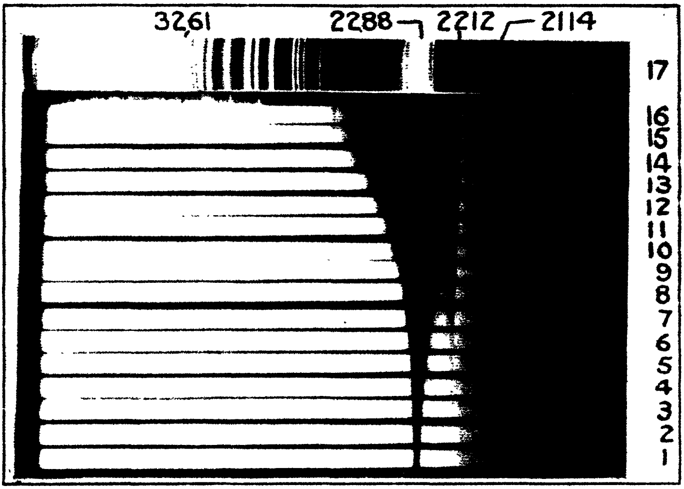


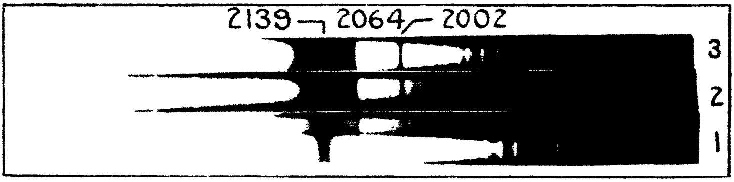
Fig. 19.

FIG. 1.



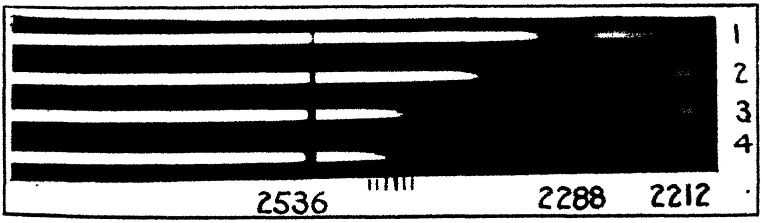
Band Spectrum of Cadmium. #1-16. Absorption Spectrum. #1, 3·3 mm.; #5, 14 mm.; #13, 95 mm.; #16, 170 mm. #17, Electrodeless Discharge in Cadmium.

FIG. 2.



Absorption Spectrum of Zinc. #1, 3 mm.; #2, 5 mm.; #3, 9 mm.

FIG. 3.



Absorption Spectrum of a Mercury-Cadmium Mixture.
For # 4, Hg at 100 mm., Cd at 60 mm.

VENKATESWARAN. Phil. Mag. Ser. 7, Vol. 7, Pl. XV.

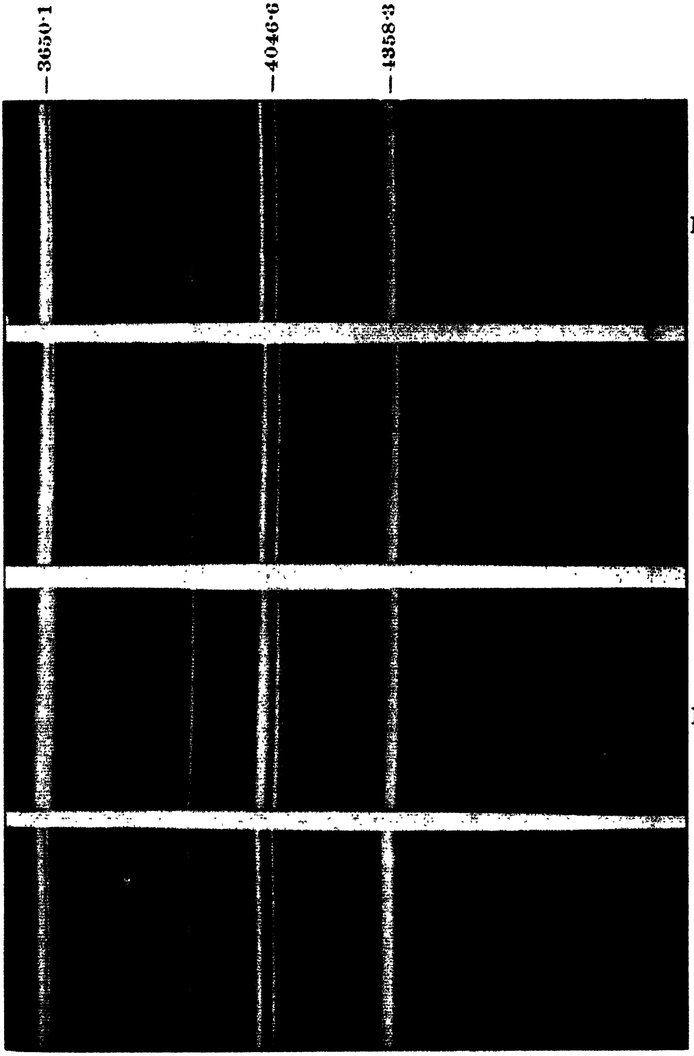


FIG. 1. Incident.

FIG. 2. Acetic acid.

FIG 3. Propionic acid.

FIG. 4. Butyric acid.

Raman Effect in Fatty Acids.

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PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

◆

[SEVENTH SERIES.]

APRIL 1929.

LXXVII. *On the Steady Motion of Viscous, Incompressible Fluids; with particular reference to a Variation Principle.*

By Clark B. Millikan, *Ph.D., Guggenheim School of Aeronautics, California Institute of Technology, U.S.A.*[*]

1. *Introduction.*

A DISCUSSION of the general equations for steady motion of a viscous, incompressible fluid from the point of view of a minimum or variation principle has, as far as the writer is aware, never been given. Helmholtz, in a classical paper[†] "On the Theory of a Stationary Flow in Viscous Liquids," has shown that if the quadratic terms in velocity be neglected, if the velocities at the boundary of a singly-connected region be kept constant, and if the external forces have a single-valued potential, then the motion is such that the variation of the energy dissipation in the region under consideration is zero. We shall refer to this work in more detail later. Korteweg subsequently showed[‡] that under the above conditions the steady motion which is set up is unique and stable, *i. e.*, the dissipation for this motion is an absolute minimum. Rayleigh[§], still later, showed that the dissipation is an absolute minimum whenever $\nabla^2\mathbf{q}=\nabla H$, where q is the vector velocity of the fluid, and H is a single-valued function subject to the condition $\nabla^2 H = 0$. In this case there is no restriction upon the magnitude of the velocity. As far as the author is aware, this represents practically the entire extent of the work to date on the application of a minimum principle to the steady motion of a viscous fluid *.

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[*] Communicated by Prof. H. Bateman, Ph.D.

[†] H. Helmholtz, 'Collected Works,' p. 223.

[‡] D. J. Korteweg, Phil. Mag. xvi. p. 112 (1883).

[§] Lord Rayleigh, Phil. Mag. xxvi. p. 776 (1913); Coll. Works, vi. p. 167.

In the present work we discuss the following problem: given an incompressible, viscous fluid with fixed (if any) boundaries, to find a function L, such that if we set

$$\delta \int_V L d\tau = 0,$$

where δ is the symbol representing variation, then the Eulerian equations corresponding to this equation are exactly the Navier-Stokes equations for the motion of the fluid. The integral is (for three-dimensional cases) a volume integral, and $d\tau$ represents the volume element. We impose, of course, the customary condition that the variation of the velocity is taken to be zero at the boundaries of the region considered. We shall for simplicity refer to such a function L as a Lagrangian function, in spite of the fact that the term is not strictly accurate.

In the second section we set up a Lagrangian function by generalizing the considerations of Helmholtz relative to slow motion, and from the resulting Eulerian equations are led to a proof of the following theorem:—

"If L be restricted to be a function of the velocity components and their first-order space derivatives only, then it is impossible to find any such L which will give the general equations for steady flow of an incompressible fluid, through the application of the variation principle described above."

The conditions which must be imposed on the motion in order that it may correspond to a variation principle, involving a Lagrangian function of this type, are discussed, and it is shown that all of the cases of steady motion which have thus far been discovered satisfy these conditions.

In the third section the Lagrangian functions are found for the cases of plane laminar motion, and Poiseuille flow through a circular tube.

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* J. Brill (Proc. Camb. Phil. Soc. viii. p. 313, 1895) has discussed a minimum principle for a case similar to that of Rayleigh. H. Bateman, in some unpublished work, has recently discussed variation principles for the general viscous equations of motion, which contain arbitrary auxiliary functions and do not in general reduce to minimum principles.

The fourth section does not strictly form a part of the general variation problem, but the results obtained in it are used in the subsequent section, and have also a certain amount of interest on their own account. Formulæ are given for the transformation of certain expressions from vector to curvilinear coordinate form, and a vector expression independent of coordinate systems is deduced for the dissipation function.

In the fifth section the variation problem for two-dimensional flow in logarithmic spirals is discussed, and the corresponding Lagrangian function is exhibited.

The analysis throughout takes no account of body forces, since, if such forces do occur and have a single-valued potential, they may be taken account of in the pressure terms, without in any way altering the form of the equations. The vector method is used whenever it appears convenient, and in such cases the notation is that of Gibbs, involving the operator ∇. Symbols denoting vector quantities are printed in bold-faced type, while the absolute value or magnitude of these quantities is denoted by the same symbols printed in normal type. In order to follow the customary use of symbols, it has been deemed advisable to change notation in the middle of the paper. In the second and third sections, involving primarily Cartesian coordinate systems, the velocity components are denoted by u, v, w. In the last two sections these symbols are used to represent curvilinear coordinates, and the velocity components are denoted by q with appropriate subscripts. The conventional subscript notation for differentiation is frequently used, the subscript 1 implying differentiation with respect to x, 2 differentiation with respect to y, etc., unless otherwise specified.

2. *On the Existence of a Lagrangian Function in General.*

We have, for steady motion of a viscous, incompressible fluid, the Navier-Stokes equations of motion, which may be combined into the single vector equation

$$\rho(\mathbf{q}\,.\,\nabla)\mathbf{q}+\nabla p=\mu\nabla^2\mathbf{q}, \quad . \quad . \quad . \quad . \quad (1)$$

where $\mathbf{q}$ represents the vector velocity of the fluid, p the pressure, ρ the density, and μ the coefficient of viscosity (the last two being assumed constant throughout this paper). In addition we have the equation of continuity,

$$\nabla\,.\,\mathbf{q}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Following Helmholtz, we define P as the rate at which work is done by the external forces (in our case pressure and viscosity forces) upon the fluid in the particular volume region we happen to discuss, and Q as the rate of dissipation of energy inside the region. We introduce a new quantity R, which we define to be the rate at which kinetic energy is carried out of the region across the boundary. We wish later to discuss the values of the above quantities per unit volume, and hence define the "density functions" **P**, **R**, **Φ** as follows:—

$$\left.\begin{aligned} \mathrm{P} &= \int_{\mathrm{V}} \mathbf{P}\, d\tau, \\ \mathrm{R} &= \int_{\mathrm{V}} \mathbf{R}\, d\tau, \\ \mathrm{Q} &= \int_{\mathrm{V}} \Phi\, d\tau, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where V is the volume region considered. Φ is usually called the dissipation function, and is given by [*]

$$\Phi = \mu\{2u_1{}^2 + 2v_2{}^2 + 2w_3{}^2 + (w_2 + v_3)^2 + (u_3 + w_1)^2 + (v_1 + u_2)^2\}, \quad . \quad . \quad . \quad (4)$$

where x, y, z are Cartesian coordinates, u, v, w are the corresponding velocity components, and the subscripts denote differentiation. This is the general expression for Φ for any viscous fluid; the condition of incompressibility has not been introduced in its derivation.

In Helmholtz case of slow motion, squares of velocity are neglected, and hence $\mathrm{R}=0$. Therefore the equation of conservation of energy is $\mathrm{P}-\mathrm{Q}=0$. Helmholtz showed that in this case, even if there are immersed bodies in the fluid so that the boundary conditions are less specified than ours, if one writes

$$\delta(\mathrm{P}-\tfrac{1}{2}\mathrm{Q}) = 0,$$

one is led to the equation of motion with quadratic terms omitted,

$$\nabla p = \mu\nabla^2 \mathrm{q}.$$

In our more general case the equation of energy becomes

$$\mathrm{P}-\mathrm{Q}-\mathrm{R} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and one is led to try as a variation principle

$$\delta(\mathrm{P}-\tfrac{1}{2}\mathrm{Q}-\gamma\mathrm{R}) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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[*] H. Lamb, 'Hydrodynamics,' 5th ed. p. 549.

where γ is a numerical coefficient to be determined empirically. We remark first that P may be written as a surface integral extended over the boundary of the region. Hence, after performing the variation, we get from this term another surface integral with components of $\delta\mathbf{q}$ as multiplying factors. But in Helmholtz's case, if we rule out immersed bodies, and in our case, the variation of velocity is assumed to be zero at the boundary. Hence the term P contributes nothing to the Eulerian equations, and may be entirely omitted in the evaluation of (6). We remark next that the variation is to be taken subject to the restriction given by the continuity equation (2). We introduce this restriction in the customary manner, namely through the use of a Lagrangian undetermined multiplier. In view of these remarks and using equations (3), we may write equation (6) in the following form :—

$$\delta\int_{\mathrm{V}}\{\tfrac{1}{2}\Phi+\gamma\mathbf{R}-\lambda\nabla\cdot\mathbf{q}\}\,d\tau=\delta\int_{\mathrm{V}}\mathrm{L}\,d\tau=0, \quad . \quad (7)$$

where λ is the Lagrangian undetermined multiplier.

In evaluating this expression it is convenient to use Cartesian coordinates. The expression for Φ is then given by equation (4), and $\mathbf{R}$ remains to be evaluated. From the definition of R we have, where S is the bounding surface of the region V, *ds* is the surface element, and $\mathbf{n}$ is a unit vector in the direction of the outwardly-drawn normal at *ds*,

$$\mathrm{R}=\frac{\rho}{2}\int_{\mathrm{S}}q^2\mathbf{n}\cdot\mathbf{q}\,ds=\frac{\rho}{2}\int_{\mathrm{S}}\mathbf{n}\cdot(q^2\mathbf{q})\,ds,$$

and applying the divergence theorem,

$$\mathrm{R}=\frac{\rho}{2}\int_{\mathrm{V}}\nabla\cdot(q^2\mathbf{q})\,d\tau=\frac{\rho}{2}\int_{\mathrm{V}}(q^2\nabla\cdot\mathbf{q}+\mathbf{q}\cdot\nabla q^2)\,d\tau,$$

and hence, because of the continuity equation,

$$\mathrm{R}=\frac{\rho}{2}\int_{\mathrm{V}}\mathbf{q}\cdot\nabla q^2\,d\tau,$$

or

$$\mathbf{R}=\frac{\rho}{2}\mathbf{q}\cdot\nabla q^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In Cartesian coordinates this gives

$$\mathbf{R}=\rho\{u^2u_1+uvv_1+uww_1+uvu_2+v^2v_2+vww_2$$
$$+uwu_3+vwv_3+w^2w_3\}.$$

Hence the function L, defined in (7), becomes

$$L = \mu\{u_1^2+v_2^2+w_3^2+\tfrac{1}{2}(w_2+v_3)^2+\tfrac{1}{2}(u_3+w_1)^2+\tfrac{1}{2}(v_1+u_2)^2\}$$
$$+\gamma\rho\{u^2u_1+uvv_1+uww_1+uvu_2+v^2v_2+vww_2$$
$$+uwu_3+vwv_3+w^2w_3\}$$
$$-\lambda\{u_1+v_2+w_3\}.$$

The Eulerian equations corresponding to equation (7) are

$$\frac{\partial}{\partial x}\left(\frac{\partial L}{\partial u_1}\right)+\frac{\partial}{\partial y}\left(\frac{\partial L}{\partial u_2}\right)+\frac{\partial}{\partial z}\left(\frac{\partial L}{\partial u_3}\right)-\frac{\partial L}{\partial u}=0,$$

with two analogous equations for v and w. Substituting our expression for L into this equation, we have

$$\mu\{2u_{11}+u_{22}+v_{12}+u_{33}+w_{13}\}$$
$$+\gamma\rho\{uv_2+uw_3-vv_1-ww_1\}-\lambda_1=0$$

(where double subscripts signify the appropriate second derivatives), or

$$\mu\left\{\nabla^2u+\frac{\partial}{\partial x}(\nabla\cdot\mathbf{q})\right\}+\gamma\rho\left\{u\nabla\cdot\mathbf{q}-\frac{1}{2}\frac{\partial q^2}{\partial x}\right\}-\frac{\partial\lambda}{\partial x}=0,$$

and introducing the continuity equation:

$$\mu\nabla^2u-\gamma\rho\frac{1}{2}\frac{\partial q^2}{\partial x}-\frac{\partial\lambda}{\partial x}=0;$$

and, finally, combining with the two analogous equations deduced from the other two Eulerian equations, we have the vector equation:

$$\gamma\rho\tfrac{1}{2}\nabla q^2+\nabla\lambda=\mu\nabla^2\mathbf{q}. \quad . \quad . \quad . \quad . \quad (9)$$

If, now, we change notation, writing p for λ, and if we take the numerical coefficient γ to be 1, then equation (9) is just the Navier-Stokes equation (1), except that $(\mathbf{q}.\nabla)\mathbf{q}$ is replaced by $\tfrac{1}{2}\nabla q^2$.

Hence, whenever conditions are imposed on the motion, of such a nature that the terms $(\mathbf{q}.\nabla)\mathbf{q}$ are replaced by $\tfrac{1}{2}\nabla q^2$, then in such cases the equations of motion may be deduced from the variation principle given in equation (6). Since we have the general vector relation

$$(\mathbf{q}.\nabla)\mathbf{q}=\tfrac{1}{2}\nabla q^2-\mathbf{q}\times\operatorname{curl}\mathbf{q},$$

we see that the condition just mentioned is satisfied in the more or less trivial case in which $\mathbf{q}\times\operatorname{curl}\mathbf{q}=0$, which implies either that the vorticity is everywhere zero, or that it is everywhere parallel to the velocity. We shall later discuss several other more interesting cases in which the condition is satisfied. At present we wish to continue with our more general considerations.

If we express $(\mathbf{q}\cdot\nabla)\mathbf{q}$ in Cartesian form, we have

$$[(\mathbf{q}\cdot\nabla)\mathbf{q}]_x = uu_1 + vu_2 + wu_3$$

(similarly for y and z components), and hence it appears that the terms in the equations of motion which the variation principle does not give are

$$vu_2,\ wu_3,\ \text{and}\ wv_3,\ uv_1,\ uw_1,\ vw_2. \quad . \quad . \quad (10)$$

We are therefore led to a consideration of the possibility of obtaining terms of this form from any Lagrangian function involving the velocity components and their first-order space derivatives. It will suffice to discuss only one of the terms mentioned, together with the single Eulerian equation corresponding to it. Then by cyclic substitution the analysis can be extended to all of the other terms. We state the problem as follows:—

" Given the Eulerian equation

$$\text{E.F.} = \frac{\partial}{\partial x}\left(\frac{\partial \text{L}}{\partial u_1}\right) + \frac{\partial}{\partial y}\left(\frac{\partial \text{L}}{\partial u_2}\right) + \frac{\partial}{\partial z}\left(\frac{\partial \text{L}}{\partial u_3}\right) - \frac{\partial \text{L}}{\partial u} = 0,$$

where we shall call the left side of this equation the 'Eulerian Function' and denote it for convenience by E.F. To find a function

$$\text{L} = \text{L}(u, v, w, u_1, u_2, u_3, v_1, v_2, v_3, w_1, w_2, w_3), \quad . \quad (11)$$

such that if we introduce this function into the Eulerian equation, we get

$$\text{E.F.} = vu_2 + t = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where t is a sum of any of the other terms in the x-component Navier-Stokes equation (1)."

It is obvious at once, since vu_2 cannot be obtained from any expression of the form $\frac{\partial f}{\partial x}$ or $\frac{\partial g}{\partial z}$, where f and g are any functions of the velocities and their space derivatives, that for the present purpose the Eulerian Function may be simplified and written :

$$\text{E.F.} = \frac{\partial}{\partial y}\left(\frac{\partial \text{L}}{\partial u_2}\right) - \frac{\partial \text{L}}{\partial u}.$$

Consider, first,

$$\text{L} = u^{\alpha} v^{\beta} w^{\gamma} u_1^{\alpha_1} u_2^{\alpha_2} u_3^{\alpha_3} v_1^{\beta_1} v_2^{\beta_2} v_3^{\beta_3} w_1^{\gamma_1} w_2^{\gamma_2} w_3^{\gamma_3}, \quad . \quad (13)$$

where the exponents are any real numbers. The Eulerian Function corresponding to this L is

$$\begin{aligned} \text{E.F.} = {} & v^{\beta}u_2^{\alpha_2}\{\alpha_2\alpha u^{\alpha-1}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3} \\ & \qquad -\alpha u^{\alpha-1}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}\} \\ & + v^{\beta}u_2^{\alpha_2-1}\{\alpha_2\gamma u^{\alpha}w^{\gamma-1}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2+1}w_3^{\gamma_3} \\ & \qquad +\alpha_2\alpha_1u^{\alpha}w^{\gamma}u_1^{\alpha_1-1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}u_{12} \\ & \qquad +\alpha_2\alpha_3u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3-1}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}u_{23} \\ & \qquad +\alpha_2\beta_1u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1-1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}v_{12} \\ & \qquad +\alpha_2\beta_2u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2-1}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}v_{22} \\ & \qquad +\alpha_2\beta_3u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3-1}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}v_{23} \\ & \qquad +\alpha_2\gamma_1u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1-1}w_2^{\gamma_2}w_3^{\gamma_3}w_{12} \\ & \qquad +\alpha_2\gamma_2u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2-1}w_3^{\gamma_3}w_{22} \\ & \qquad +\alpha_2\gamma_3u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3-1}w_{23}\} \\ & + \quad v^{\beta}u_2^{\alpha_2-2}\{\alpha_2(\alpha_2-1)u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3}u_{22}\} \\ & + v^{\beta-1}u_2^{\alpha_2-1}\{\alpha_2\beta u^{\alpha}w^{\gamma}u_1^{\alpha_1}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2+1}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_2^{\gamma_3}\}. \end{aligned} \quad . \quad . \quad . \quad (14)$$

From this equation it appears that there are four possible combinations of values of β and α_2 which could give vu_2 :—

(1) $\beta=\alpha_2=1$. In this case the terms in the bracket multiplying vu_2 cancel, and the entire term involving vu_2 vanishes.

(2) $\beta=1$, $\alpha_2=3$. Here there is a factor u_{22} multiplying vu_2 which cannot be made to disappear. Hence this combination does not give an expression of the form (12).

(3) $\beta=\alpha_2=2$. In this case the additional conditions that we get a term of the form vu_2 are

$$\alpha=\gamma=\alpha_1=\alpha_3=\beta_1=\beta_3=\gamma_1=\gamma_2=\gamma_3=0, \quad \beta_2=-1.$$

Hence

$$\text{L}=\frac{v^2u_2^2}{v_2},$$

and the Eulerian Function becomes

$$\text{E.F.}=4vu_2+2\frac{v^2}{v_2}u_{22}-2\frac{v^2u_2}{v_2^2}v_{22}.$$

The last two terms of this expression do not appear in the equations of motion. Hence we must find a second function L′ to be subtracted from L, where L′ gives these extraneous terms. But both of these terms have second derivatives as multiplying factors, and from (14) we see that any such term involving second derivatives occurs in the Eulerian Function in a single, unique manner ; *i. e.*, the only function L′ leading to either of these terms is precisely the function L which we have already found. Therefore, in this third case also, it is impossible to get an Eulerian Function of the required form (12).

(4) $\beta=1$, $\alpha_2=2$. The additional conditions are here

$$\alpha=\alpha_1=\alpha_3=\beta_1=\beta_2=\beta_3=\gamma_1=\gamma_3=0, \quad \gamma=1, \quad \gamma_2=-1.$$

Hence

$$L=\frac{vwu_2^2}{w_2}$$

and

$$E.F. = 2vu_2-2\frac{vwu_2}{w_2^2}w_{22}+2\frac{vw}{w_2}u_{22}+2\frac{wu_2v_2}{w_2}.$$

Here we have three extraneous terms. To the first two we apply the same argument as we did in case (3), and conclude that in this case also it is impossible to get an Eulerian Function of the form (12).

Collecting the results of the four possible cases, we may conclude that with a Lagrangian function of the form (13) it is impossible to get an Eulerian Function of the form (12). This result can at once be somewhat generalized as follows. It is obvious that it is impossible to get an Eulerian Function of the form (12) from a Lagrangian function composed of any sum of terms of the form (13). If, now, we define a new variable,

$$z=u^{\alpha}v^{\beta}w^{\gamma}u_1^{\alpha_1}u_2^{\alpha_2}u_3^{\alpha_3}v_1^{\beta_1}v_2^{\beta_2}v_3^{\beta_3}w_1^{\gamma_1}w_2^{\gamma_2}w_3^{\gamma_3},$$

then for any function

$$L=L(u, v, \ldots, w_2, w_3),$$

which has no singularity inside the volume region under consideration, a series

$$S=\sum_{-\infty}^{\infty} c_i z^i$$

can be found which converges uniformly to the function L inside the region. But we have seen that no Lagrangian function of the form $\Sigma c_i z^i$ satisfies our condition of leading to an Eulerian Function of the form (12). Hence no

Lagrangian function of the form (11), which has no singularities in the region considered, can be found which satisfies our condition. But Lagrangian functions involving singularities inside the region in which the fluid motion is taking place are ruled out for physical reasons. Finally, by cyclic substitution we find that all of the above results are valid when any of the expressions of (10) are substituted for vu_2 if only we use the Eulerian equation corresponding. Hence the theorem stated in the introduction has been proved. We shall here restate it in a different form, employing the conditions mentioned in the first section.

"It is impossible to derive the equations of steady motion of a viscous, incompressible fluid from a variation principle involving as Lagrangian function an expression in the velocity components and their first-order space derivatives, unless conditions are imposed on these velocity components such that all of the terms vu_2, wu_3, wv_3, uv_1, uw_1, vw_2 disappear from their positions in the Navier-Stokes equations." This disappearance may arise either because the terms vanish identically, or because they are replaced (according to the imposed conditions) by other expressions not so intractable. We shall refer to cases in which such conditions are satisfied as "exceptional cases." It should be noticed that the equations of motion may still be deduced from our variation principle, even though the intractable terms appear, if the latter occur in other of the component Navier-Stokes equations from those which they occupy in general. For example, if our imposed conditions allowed us to replace vu_2 by uv_1 in the x-component Navier-Stokes equation, then the function $L=uvu_1$, substituted in the Eulerian Function corresponding to this x-component, *i. e.* in

$$\frac{\partial}{\partial x}\left(\frac{\partial L}{\partial u_1}\right)+\frac{\partial}{\partial y}\left(\frac{\partial L}{\partial u_2}\right)+\frac{\partial}{\partial z}\left(\frac{\partial L}{\partial u_3}\right)-\frac{\partial L}{\partial u},$$

would give the "intractable" term uv_1. However, such examples still fall under the class of "exceptional cases," for some imposed condition on the velocities is necessary in order to transform the equations of motion into a form in which they may be deduced from our variation principle.

The above theorem may also be formulated from the point of view of a minimum instead of a variation principle: "Except in the 'exceptional cases' there is no function of the velocity components, their first-order space derivatives (and possibly the space coordinates), which is a minimum for the steady motion of a viscous, incompressible fluid."

We proceed with a discussion of various examples of the "exceptional cases" for which steady solutions have been found. There are essentially only three such cases existing for viscous fluids. One is motion in which the entire fluid moves as a rigid body with uniform rotation. In this case we may write

$$u = cy, \qquad v = -cx,$$

so that

$$2vu_2 = -2vv_1 = -\frac{\partial}{\partial x}(v^2) = -\frac{\partial}{\partial x}(u^2+v^2) = -\frac{\partial}{\partial x}q^2,$$

$$2uv_1 = -2uu_2 = -\frac{\partial}{\partial y}q^2,$$

$$\therefore \quad (\mathbf{q}\cdot\nabla)\mathbf{q} = -\tfrac{1}{2}\nabla q^2,$$

and we have the particular example of an "exceptional case" previously discussed explicitly. The second case includes plane laminar flow and Poiseuille flow in a tube of uniform cross-section. In both of these cases we can choose a set of rectangular axes such that two components of velocity vanish throughout the fluid. Hence we have the exceptional case in which the intractable terms vanish identically. Finally, there is Hamel's case of flow in logarithmic spirals, which will be discussed in detail in section 5. Here there is only one non-vanishing component of velocity relative to a set of orthogonal curvilinear coordinates, and in the one component Navier-Stokes equation which remains to determine the velocity, the component of $(\mathbf{q}\cdot\nabla)\mathbf{q}$ is replaced by the corresponding component of $\frac{1}{2}\nabla q^2$, so that the "exceptional case" is similar to that explicitly mentioned immediately following equation (9).

Hence all of the cases of steady motion thus far discovered belong to the class of "exceptional cases," and it should be possible to find Lagrangian functions for all of them.

3. *The Lagrangian Functions for Plane Laminar and Poiseuille Flow.*

For the discussion of plane laminar flow we choose Cartesian coordinates and assume two-dimensional motion, writing

$$w = \frac{\partial}{\partial z} = 0.$$

In general it will be convenient, when discussing two-dimensional motion, to retain the three-dimensional language as to volume and surface elements, introducing a unit length in the z direction to complete the three dimensions; *i. e.*,

$$d\tau = dx\,dy\,.1,$$

$$\int_S ds = \text{line integral in the } x, y \text{ plane.}$$

We consider flow between two parallel walls $x=x_1$ and $x=x_2$, and take a region bounded by these two walls and any two perpendicular planes $y=y_1$ and $y=y_2$ (and by two planes $z=z_1$ and $z=z_2$ unit distance apart). Then, introducing the usual restriction on the motion,

$$q = u, \qquad v = 0,$$

and the continuity equation gives

$$u_1 = 0 \quad \text{or} \quad u = u(y).$$

The Navier-Stokes equations reduce to the following single equation for the determination of u in terms of the pressure gradient:

$$\mu u_{22} - \frac{\partial p}{\partial x} = 0. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In this case the flux of kinetic energy out of our region is zero, *i. e.* R=0. Hence the equation of conservation of energy takes Helmholtz's simplified form (see equation (5)):

$$\mathrm{P} - \mathrm{Q} = 0,$$

and we expect Helmholtz's result to hold, namely

$$\delta(\mathrm{P} - \tfrac{1}{2}\mathrm{Q}) = 0.$$

This equation is found to be valid; in fact Rayleigh has shown [*] that Q is an absolute minimum. However, if we take the dissipation function Φ as Lagrangian function, we do not get the equation of motion (16) from our variation principle.

In order to find the proper Lagrangian function we must somewhat alter the procedure followed in section 2. The difficulty is that here we have already introduced the continuity equation explicitly, and consequently cannot introduce an arbitrary multiplier λ into the variation equation, which multiplier is later to be identified with the pressure p. We must find some other way of bringing p into the Lagrangian function. The method adopted appears to be the one which must be employed in general, whenever the continuity equation has been explicitly used to restrict the nature of the velocity components. The method is the following. Instead of considering P as a surface integral and as having, therefore, no effect on the variation problem, we transform P to a volume integral, just as we previously transformed R, and incorporate the "density function" **P** in the Lagrangian function. Since at the walls the velocity is zero, according to the customary assumption of no slip, there is no work done on the fluid in our region due to viscous forces acting across these boundaries. Obviously no work is done by any tractions across the planes $z=z_1$ and $z=z_2$. Since the velocity is normal to the other boundaries $y=y_1$ and $y=y_2$, the only work done on the region is due to pressure forces, and we may write (n = outwardly drawn normal),

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[*] *Loc. cit.*

$$\mathrm{P} = -\int_S p\mathbf{n}.\mathbf{q}\,ds = -\int_S \mathbf{n}.p\mathbf{q}\,ds,$$

and applying the divergence theorem

$$\mathrm{P} = -\int_V \nabla.p\mathbf{q}\,d\tau = -\iint \frac{\partial}{\partial x}(pu)\,dx\,dy,$$

and, finally, since $u=u(y)$,

$$\mathrm{P} = -\int_V u\frac{\partial p}{\partial x}\,d\tau.$$

$$\therefore\quad \mathbf{P} = -u\frac{\partial p}{\partial x}.$$

From equation (4)

$$\Phi = \mu u_2^2,$$

and hence the variation principle (6) becomes for this case

$$\left.\begin{array}{c} \delta(\mathrm{P}-\tfrac{1}{2}\mathrm{Q}) = 0 \\ \text{or}\quad \delta\iint_V \left\{\dfrac{\mu}{2}u_2^2 + u\dfrac{\partial p}{\partial x}\right\} dx\,dy = 0. \end{array}\right\} \quad . \quad . \quad (17)$$

The Eulerian equation gives

$$\mu u_{22} - \frac{\partial p}{\partial x} = 0,$$

which is exactly the equation of motion (16).

Hence for plane laminar flow we have verified the fact that the correct Lagrangian function, giving the equations of motion by a variation principle, is

$$\mathrm{L} = \mathbf{P} - \tfrac{1}{2}\Phi - \mathbf{R}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

in agreement with (6). In this particular case, since $\mathbf{R}=0$, we have

$$L_{\text{plane laminar}} = \mathbf{P}-\tfrac{1}{2}\Phi. \quad . \quad . \quad . \quad . \qquad (19)$$

The case of Poiseuille flow in a tube is obviously exactly the same in principle as the above. The imposed conditions imply that all but one component of velocity vanish, so that if the x axis is parallel to the axis of the tube,

$$q = q_x = u.$$

Then the continuity equation imposes the additional restriction that u is independent of x and is a function of a single parameter of the nature of the distance from the axis, so that the Navier-Stokes equations reduce to a single one determining u as a function of this parameter. R vanishes exactly as above, and $\mathbf{P}$ has obviously the same value: $\mathbf{P}=-u\dfrac{\partial p}{\partial x}$, so that the only problem in finding L is to express Φ in the proper coordinates. In the case of a circular tube, for example, where we define r as the distance from the axis,

$$u = u(r),$$

$$\Phi = \mu\left(\frac{\partial u}{\partial r}\right)^2,$$

and

$$L = \mathbf{P}-\tfrac{1}{2}\Phi = -\left\{\tfrac{1}{2}\mu\left(\frac{\partial u}{\partial r}\right)^2 + u\frac{\partial p}{\partial x}\right\}.$$

Hence the variation principle takes the form:

$$\delta\int_V L\,d\tau = \delta\int_0^{2\pi}\int_{x_1}^{x_2}\int_0^{r_0}\left\{\tfrac{1}{2}\mu\left(\frac{\partial u}{\partial r}\right)^2 + u\frac{\partial p}{\partial x}\right\} r\,dr\,dx\,d\theta = 0,$$

where r_0=radius of the tube, or

$$2\pi(x_2-x_1)\,\delta\int_0^{r_0}\left\{\frac{\mu r}{2}\left(\frac{\partial u}{\partial r}\right)^2 + ur\frac{\partial p}{\partial x}\right\} dr = \delta\int_0^{r_0} L_0\,dr = 0,$$

where

$$L_0 = 2\pi(x_2-x_1)rL.$$

The Eulerian equation $\left(\text{writing } u'=\dfrac{\partial u}{\partial r}\right)$

$$\frac{\partial}{\partial r}\left(\frac{\partial L_0}{\partial u'}\right) - \frac{\partial L_0}{\partial u} = 0$$

gives
$$\mu\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right)-r\frac{\partial p}{\partial x}=0$$
or
$$\frac{1}{\mu}\frac{\partial p}{\partial x}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right),$$
which is exactly the Navier-Stokes equation for $u(r)$.

Hence the results of this case are identical with those for the previous one as far as the form of the Lagrangian function is concerned. A new element which has appeared, however, is one which we shall find again in section 5, namely: if curvilinear coordinates are employed then, in writing the Eulerian equations, the functions of coordinates introduced through the transformation from a Cartesian to a curvilinear system, must be taken into account.

The results of this section have been to verify, for some special cases, the correctness of the variation principle given in (6), and to demonstrate the fact that if the continuity equation be introduced to give an explicit limitation on the velocity components, then, in getting the Lagrangian function, P must be considered as a volume integral and must be included in performing the variations.

4. *Certain Vector and Curvilinear Coordinate Relations.*

In this section a few relations are given, both because they are required for the analysis of the subsequent section and also because they have a certain amount of interest *per se*. As mentioned in the introduction, it is convenient to change notation at this point, using u, v, w to denote families of orthogonal curvilinear coordinates, while the corresponding velocity components are given by q_u, q_v, q_w. In terms of Cartesian coordinates we have

$$u=u(x,y,z)\ ;\quad v=v(x,y,z)\ ;\quad w=w(x,y,z).$$

Then, if ds represents the line element, we define the quantities U, V, W by

$$ds^2=\mathrm{U}^2du^2+\mathrm{V}^2dv^2+\mathrm{W}^2dw^2,$$

where

$$\mathrm{U}=\mathrm{U}(u,v,w)\ ;\quad \mathrm{V}=\mathrm{V}(u,v,w)\ ;\quad \mathrm{W}=\mathrm{W}(u,v,w).$$

Then the volume element becomes

$$d\tau=\mathrm{UVW}\,du\,dv\,dw.$$

Unit vectors in the directions of increasing u, v, w respectively are denoted by $\mathbf{i}_u$, $\mathbf{i}_v$, $\mathbf{i}_w$ (at any point u, v, w in the space). The expressions for $\nabla\phi$, $\nabla\cdot\mathbf{A}$, $\nabla^2\phi$, and $\nabla\times\mathbf{A}$, where ϕ represents an arbitrary scalar and $\mathbf{A}$ an arbitrary vector, in terms of such a coordinate system, are given in many standard mathematical and physical works. In addition to these we shall require the curvilinear coordinate expressions for $\nabla^2\mathbf{A}$ and $(\mathbf{A}.\nabla)\mathbf{A}$. By elementary vector analysis these may be deduced from the above-mentioned standard expressions. The following formulæ, which the author has been unable to find in any work with which he is acquainted, have been obtained in this way :—

$$\left.\begin{aligned}
&\nabla^2\mathbf{A}\\
&=\left\{\frac{1}{U}\frac{\partial}{\partial u}(\nabla.\mathbf{A})+\frac{1}{VW}\left[\frac{\partial}{\partial w}\left\{\frac{V}{WU}\left(\frac{\partial UA_u}{\partial w}-\frac{\partial WA_w}{\partial u}\right)\right\}\right.\right.\\
&\qquad\qquad\left.\left.-\frac{\partial}{\partial v}\left\{\frac{W}{UV}\left(\frac{\partial VA_v}{\partial u}-\frac{\partial UA_u}{\partial v}\right)\right\}\right]\right\}\mathbf{i}_u\\
&+\left\{\frac{1}{V}\frac{\partial}{\partial v}(\nabla.\mathbf{A})+\frac{1}{WU}\left[\frac{\partial}{\partial u}\left\{\frac{W}{UV}\left(\frac{\partial VA_v}{\partial u}-\frac{\partial UA_u}{\partial v}\right)\right\}\right.\right.\\
&\qquad\qquad\left.\left.-\frac{\partial}{\partial w}\left\{\frac{U}{VW}\left(\frac{\partial WA_w}{\partial v}-\frac{\partial VA_v}{\partial w}\right)\right\}\right]\right\}\mathbf{i}_v\\
&+\left\{\frac{1}{W}\frac{\partial}{\partial w}(\nabla.\mathbf{A})+\frac{1}{UV}\left[\frac{\partial}{\partial v}\left\{\frac{U}{VW}\left(\frac{\partial WA_w}{\partial v}-\frac{\partial VA_v}{\partial w}\right)\right\}\right.\right.\\
&\qquad\qquad\left.\left.-\frac{\partial}{\partial u}\left\{\frac{V}{WU}\left(\frac{\partial UA_u}{\partial w}-\frac{\partial WA_w}{\partial u}\right)\right\}\right]\right\}\mathbf{i}_w,\\
&(\mathbf{A}.\nabla)\mathbf{A}\\
&=\left\{\frac{1}{2U}\frac{\partial A^2}{\partial u}-\frac{A_v}{UV}\left(\frac{\partial VA_v}{\partial u}-\frac{\partial UA}{\partial v}\right)\right.\\
&\qquad\qquad\left.+\frac{A_w}{WU}\left(\frac{\partial UA_u}{\partial w}-\frac{\partial WA_w}{\partial u}\right)\right\}\mathbf{i}_u\\
&+\left\{\frac{1}{2V}\frac{\partial A^2}{\partial v}-\frac{A_w}{VW}\left(\frac{\partial WA_w}{\partial v}-\frac{\partial VA_v}{\partial w}\right)\right.\\
&\qquad\qquad\left.+\frac{A_u}{UV}\left(\frac{\partial VA_v}{\partial u}-\frac{\partial UA_u}{\partial v}\right)\right\}\mathbf{i}_v\\
&+\left\{\frac{1}{2W}\frac{\partial A^2}{\partial w}-\frac{A_u}{WU}\left(\frac{\partial UA_u}{\partial w}-\frac{\partial WA_w}{\partial u}\right)\right.\\
&\qquad\qquad\left.+\frac{A_v}{VW}\left(\frac{\partial WA_w}{\partial v}-\frac{\partial VA_v}{\partial w}\right)\right\}\mathbf{i}_w.
\end{aligned}\right\} \quad . \; . \; . \quad (20)$$

Using the above formulæ it is easy to express the Navier-Stokes equations in terms of any curvilinear orthogonal coordinate system. However, in searching for Lagrangian functions it is necessary to have the dissipation function Φ expressed in a similar way. The simplest method of accomplishing this appears to be to first obtain an expression for Φ involving only vectors, and hence entirely independent of coordinate systems, and then to use the above transformation formulæ to get the final form desired. There is also some interest for other purposes in having an expression for Φ independent of any coordinate system. The calculation of the transformation from the Cartesian form of (4) to the vector form is somewhat lengthy, so that only the final result, which can immediately be verified, is given here[*] :

$$\Phi = \mu\{\nabla^2 q^2 - (\nabla \times \mathbf{q})^2 - 2\mathbf{q} . \nabla^2 \mathbf{q}\}. \quad . \quad . \quad (21)$$

It should be noted that the condition of incompressibility has not been introduced in the derivation of this expression, so that it is valid for any viscous fluid.

5. *The Lagrangian Function for Logarithmic Spiral Flow.*

In a recent paper[†] Hamel has given a very elegant discussion of a new general type of steady motion of an incompressible fluid. He considers a two-dimensional motion in which the streamlines are restricted to coincide with an isometric family of curves. He then proves that this family must necessarily be a set of logarithmic spirals. In discussing this type of motion here it is convenient to employ a notation different from that of Hamel, which was used by the present writer in some recent work on the same subject[‡]. This notation is in part identical with that of the previous section.

Since we are dealing with two-dimensional motion, we take

$$\frac{\partial}{\partial w} = 0, \quad \mathrm{W} = 1, \quad q_w = 0,$$

and define

$$u + iv = \pi(x + iy) = \pi(z),$$

where π is a function of the complex variable $z = x + iy$.

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[*] The details of the transformation are given in an unpublished thesis by the author; California Institute of Technology, 1928.

[†] *Deutsche Mathematiker-Vereinigung*, xxv. p. 34.

[‡] Appearing in a current issue of the *Mathematische Annalen*.

This imposes the restriction $V=U$, and implies that u=constant and v=constant constitute two orthogonal families of isometric curves. We assume that the velocity of the fluid is everywhere tangent to the family u=constant, *i. e.* the streamlines coincide with this family.

$$\therefore \quad q=q_u, \quad q_v=0.$$

The continuity equation for an incompressible fluid gives at once

$$q=\frac{f(v)}{U},$$

where f is an arbitrary function of v. Introducing all of these restrictions, and using equations (20), the Navier-Stokes equations (1) for this case reduce to

$$\left.\begin{aligned}\frac{\partial p}{\partial u}&=-\frac{\rho}{2}f^2\frac{\partial}{\partial u}(1/U^2)+\mu\frac{\partial}{\partial v}(f'/U^2),\\ \frac{\partial p}{\partial v}&=-\frac{\rho}{2}f^2\frac{\partial}{\partial v}(1/U^2)-\mu f'\frac{\partial}{\partial u}(1/U^2),\end{aligned}\right\} \quad . \quad . \quad (22)$$

where primes denote differentiation with respect to v.

In the work cited above it is proved from these equations that the curves u=constant and v=constant must necessarily coincide with the following orthogonal families of logarithmic spirals :

$$\left.\begin{aligned}u&=b\log r-a\theta,\\ v&=a\log r+b\theta,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where r, θ are polar coordinates and a, b are arbitrary real constants. Plane radial and Couette flow are given as the two limiting cases for $a=0$ and $b=0$ respectively. It is convenient to introduce two new real constants A and B, where

$$A=\frac{2b}{a^2+b^2}, \qquad B=\frac{2a}{a^2+b^2}.$$

Then it has been shown that

$$U^2=e^{Au+Bv}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The differential equation for f, which might be called the equation of motion, is obtained by eliminating p from equations (22) and substituting the above value of U^2 into the resulting equation. This gives

$$A\rho ff'+\mu\{(A^2+B^2)f'-2Bf''+f'''\}=0,$$

or integrating once and writing $\frac{\mu}{\rho} = \nu =$ coefficient of kinematic viscosity,

$$f'' - 2Bf' + (A^2 + B^2)f + \frac{A}{2\nu}f^2 = \alpha, \quad . \quad . \quad (25)$$

where α is an arbitrary constant of integration.

The problem is now to find a Lagrangian function which will give the "equation of motion" (25) through the application of a variation principle. For the region over which to integrate we make a similar choice to that of section 3, *i. e.* we take z boundaries unit distance apart. We consider flow between fixed walls which coincide with two members of the chosen family of logarithmic spirals, and take these two walls $u = u_1$ and $u = u_2$ as boundaries of our region. The other two boundaries are formed by any two members of the orthogonal family of curves, $v = v_1$ and $v = v_2$. Notice that in any particular problem u_1 and u_2 are specified, while v_1 and v_2 are arbitrary. We assume $\delta q = 0$ at all these boundaries and search for a Lagrangian function L such that, if we set

$$\delta \int_V L\, d\tau = 0,$$

where V is the region specified, then the Eulerian equation is (25). From the general results of the first section it is to be expected that the variation principle will be of the form *i.e.* (6),

$$\delta \int_V L\, d\tau \overset{?}{=} \delta(P - \tfrac{1}{2}Q - \gamma R). \quad . \quad . \quad . \quad (26)$$

However, in connexion with this particular case two remarks must be made. First, since the continuity equation has been explicitly introduced in the expression for velocity components, we expect from section 3 that P must be considered as a volume integral and included in the variation. Second, since we have chosen a particular set of coordinates, and since this choice has introduced certain restrictions, we may expect certain functions of the coordinates to appear in the right-hand member of (26). For the same reason the numerical factor γ, which appears in that member, may not be unity, as was found in the second section to be the case in general. For these reasons it will be convenient to first try

$$L = L' \equiv \mathbf{P} - \tfrac{1}{2}\Phi - \gamma\mathbf{R}, \quad . \quad . \quad . \quad . \quad (27)$$

remembering that it may be necessary to introduce some function of the coordinates into the right-hand member in order that the Eulerian equation give the equation of motion (25).

In evaluating **P**, the conditions are essentially the same as for plane laminar flow, and for the same reasons as mentioned in section 3 the work of the external forces is entirely due to pressure forces. (Notice that the velocity is perpendicular to the boundaries $v=v_1$ and $v=v_2$.) As in that section, we retain the three-dimensional language, but omit the z variable as having no effect on the equations. Hence

$$\mathrm{P} = -\int_{\mathrm{S}} p\mathbf{n}.\mathbf{q}\,ds = -\int_{\mathrm{V}} \mathbf{q}.\nabla p\,d\tau,$$

$$\mathbf{P} = -\mathbf{q}.\nabla p = -q_u \frac{1}{\mathrm{U}}\frac{\partial p}{\partial u},$$

$$\therefore \quad \mathbf{P} = -\frac{f}{\mathrm{U}^2}\frac{\partial p}{\partial u}. \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

Since the pressure p has been eliminated in the equation of motion (25) which we are trying to obtain, and the arbitrary constant α has been introduced, hence in (28) we must replace $\frac{\partial p}{\partial u}$ by an expression involving the velocity, its first derivatives, and α. To do this we go back to the equations of motion as given in (22). Here $\frac{\partial p}{\partial u}$ is given in terms of f and f''. The f'' is eliminated by using (25). Eliminating f'' in this way and introducing the value for U^2 given in (24), we get

$$\frac{\partial p}{\partial u} = -\frac{\mu}{\mathrm{U}^2}\{(\mathrm{A}^2+\mathrm{B}^2)f - \mathrm{B}f' - \alpha\},$$

so that, finally,

$$\mathbf{P} = \frac{\mu}{\mathrm{U}^4}\{(\mathrm{A}^2+\mathrm{B}^2)f^2 - \mathrm{B}ff' - \alpha f\}. \quad . \quad . \quad . \qquad (29)$$

The general expression for **R** given in (8) holds in this case, so that

$$\mathbf{R} = \frac{\rho}{2}\mathbf{q}.\nabla q^2 = \frac{\rho}{2}\frac{f}{\mathrm{U}^2}\frac{\partial}{\partial u}\left(\frac{f^2}{\mathrm{U}^2}\right) = \frac{\rho}{2\mathrm{U}^2}f^3\frac{\partial}{\partial u}\left(\frac{1}{\mathrm{U}^2}\right),$$

$$\therefore \quad \mathbf{R} = -\frac{1}{\mathrm{U}^4}\frac{\rho}{2}\mathrm{A}f^3. \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

Using the standard transformation formulæ and equations (20) to express Φ as given in (21) in terms of our particular coordinate system, we have, after a little calculation,

$$\Phi = \frac{\mu}{U^4}\{(A^2+B^2)f^2-2Bff'+f'^2\}. \quad . \quad . \quad (31)$$

Hence, from (27),

$$L' = e^{-2(Au+Bv)}\left\{\mu\left(\frac{A^2+B^2}{2}f^2-\alpha f-\tfrac{1}{2}f'^2\right)+\frac{\gamma}{2}\rho Af^3\right\}. \quad (32)$$

We remarked in section 3 that it was necessary to form a function L_0 (obtained by multiplying L by the Jacobian of the transformation from Cartesian to curvilinear coordinates) to use instead of L in setting up the Eulerian equation. This is a general rule for carrying out a variation principle in any curvilinear coordinates. In our case we have

$$\delta\int_V L\,d\tau = \delta\iint_V LU^2\,du\,dv = \delta\iint_V L_0\,du\,dv = 0,$$

and the Eulerian equation is

$$\frac{\partial}{\partial v}\left(\frac{\partial L_0}{\partial f'}\right)-\frac{\partial L_0}{\partial f} = 0.$$

If we take $L=L'$ as defined in (32), this does not give the equation of motion (25), and it appears that, in order to get the result we are seeking, we must set

$$L = \frac{L'}{U^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Then $L_0=LU^2=L'$, and the Eulerian equation becomes

$$\frac{\partial}{\partial v}\left(\frac{\partial L'}{\partial f'}\right)-\frac{\partial L'}{\partial f} = 0,$$

which gives

$$f''-2Bf'+(A^2+B^2)f+\frac{3\gamma}{2\nu}Af^2 = \alpha,$$

which is exactly the equation of motion (25) if $\gamma=\frac{1}{3}$.

Hence, as we suspected, the introduction of a particular coordinate system may alter the general expression for L. In the case of logarithmic spiral flow this alteration consists in changing L from the invariant function

$$L = \mathbf{P}-\tfrac{1}{2}\Phi-\gamma\mathbf{R}$$

to the expression depending on the coordinate system

$$L = (\mathbf{P}-\tfrac{1}{2}\Phi-\gamma\mathbf{R})\frac{1}{U^2}, \quad . \quad . \quad . \quad . \quad (34)$$

where γ has the value $\frac{1}{2}$ instead of 1, and U^2 is the Jacobian of the transformation from Cartesian to logarithmic spiral coordinates.

6. *Conclusions.*

The results of this paper, in so far as they relate to a variation principle, may be summarized as follows:—

(1) Except in certain "exceptional cases" the equations of steady motion of a viscous, incompressible fluid cannot be deduced from a variation principle involving a Lagrangian function containing only the velocity components, their first-order space derivatives, and possibly functions of the coordinates.

(2) All the cases of such motion which have yet been discovered belong to this class of "exceptional cases," and the corresponding variation principles may be found.

(3) The Lagrangian functions for these cases are exhibited and the corresponding variation principles are found to be all of the form $\delta(P-\frac{1}{2}Q-\gamma R)=0$, except for functions of coordinates, which may be introduced through the imposing of restrictions on the velocity by the coordinate system chosen to describe the motion.

In conclusion, the author wishes to express his deep appreciation of the continued assistance and inspiration of Prof. H. Bateman, who originally suggested the problem and offered many valuable suggestions during its progress.

Norman Bridge Laboratory,
October 1928.

LXXVIII. *A New Method of Measuring the Electrical Resistances of Alloys.* *By* A. L. Norbury, *D.Sc., The British Cast-Iron Research Association (Birmingham)* [*].

Introduction.

THE present work was commenced with the idea of measuring the diameters of Brinell [†] impressions, while the load was on, by measuring the electrical resistance of a circuit comprising the Brinell ball and the specimen under test. An increase in the diameter of the impression produced should decrease the electrical resistance of the above circuit; consequently it should be possible to measure diameters in terms of electrical resistance. It was found, however, that the specific electrical resistance of the material tested influenced the results obtained. Consequently the method may be used to measure the specific electrical resistance of alloys by measuring the electrical resistance in the Brinell ball circuit, measuring the diameter of the

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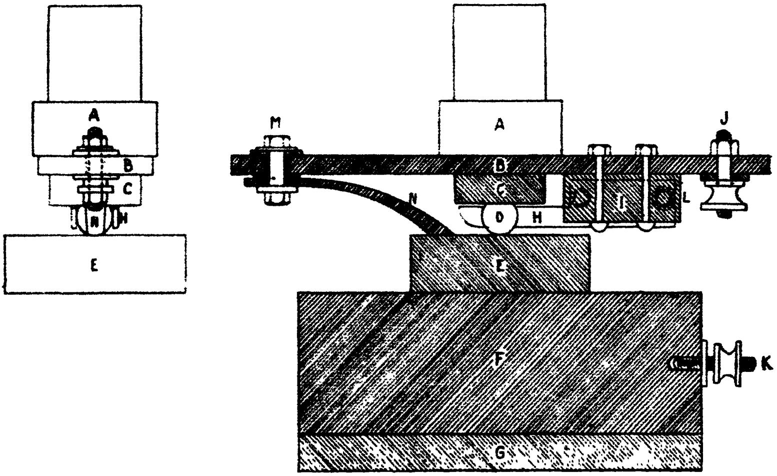
[*] Communicated by the Author.

[†] The Brinell hardness test consists in pressing a 10-mm. hardened steel ball into the material under test by means of a known load for 30 seconds. The diameter of the resulting impression is measured with a microscope, and the Brinell hardness number is obtained by dividing the load applied by the spherical area of the impression produced.

Fig. 1 *a*.



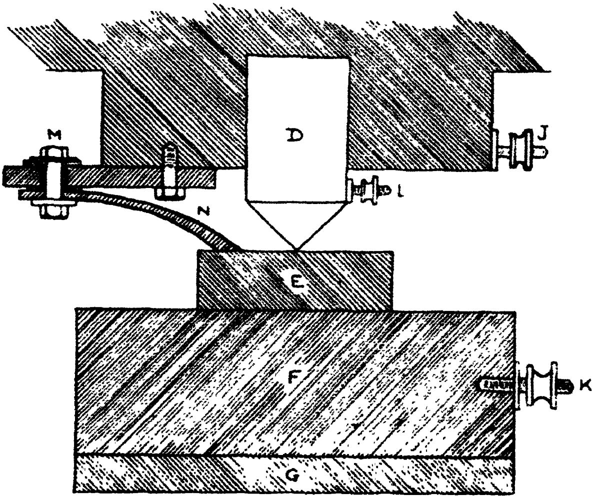
Measurement of drop of potential between equator of 10-mm. ball and surface of specimen.

A. Mild steel holder for attaching to Brinell machine.
B. Mild steel plate screwed on to A in fig. 1 *a* and on to Brinell machine in fig. 1 *b*.
C. Hardened steel disk.
D. 10-mm. ball-bearing ground flat on top in fig. 1 *a* and a 90° cone in fig. 1 *b*.
E. Specimen under test.
F. Mild steel table.
G. Uralite asbestos sheet insulator.
H. Two hardened steel strips making contact with 10-mm. ball at its equator.
I. Vulcanite block for insulating H from B.
J & K. Terminals for accumulator current.
L. Terminal for P.D. contact at equator of 10-mm. ball in fig. 1 *a*. Soldered on to shoulder of 90° cone in fig. 1 *b*.
M. Terminal insulated from B for P.D. contact N.
N. Cold-hammered copper P.D. contact pressing on to surface of specimen.

impression produced, and interpreting the results by means of calibration curves. Conversely, knowing the specific electrical resistance of the material under test, the size of the Brinell impression can be obtained. Similar tests were carried out, using 90° cones of steel and copper. The method makes it possible to measure the specific electrical resistance of alloys of any shape or size, provided a plane surface about 5 mm. by 5 mm. or larger is available.

The apparatus shown in figs. 1 *a* and 1 *b* was developed for this purpose. A current of 2 or 3 amperes was passed through the circuit, and the drop of potential between the equator of the ball or shoulder of the 90° cone and the surface of the specimen was compared on a Tinsley vernier potentiometer with the drop of potential across a standard resistance in the same circuit.

Fig. 1 *b*



Measurement of drop of potential between shoulder of 90° cone and surface of specimen

[For explanation of lettering see fig. 1 *a*.]

Elimination of Contact Resistance between Ball and Specimen under Test.

At first very erratic drop of potential results were obtained, due to bad electrical contact, caused by the presence of vaseline, oil, emery powder, etc., between the 10-mm. ball and the impression. With a vaselined ball the drop of potential was as much as ten times too great, and would gradually decrease with time as the vaseline was squeezed out from between the ball and the impression. Tests were then made on specimens freshly polished with No. 0 emery paper and washed (as was the 10-mm. ball) with methylated spirits. The results obtained in this way were moderately satisfactory, and could be repeated to within about 10 per cent. Further experiments showed that the drop of potential measured as above was still high on account of contact resistance, and that it was necessary to etch the specimen and ball and wash and dry them with methylated spirits just before making an impression. When this was done, very consistent and accurate results were obtained. Etching removed grease, particles of emery, etc., very effectively, and thereby ensured perfect electric contact between the specimen and the impressed Brinell ball.

Electrical Resistance Results, using a 10-mm. Ball.

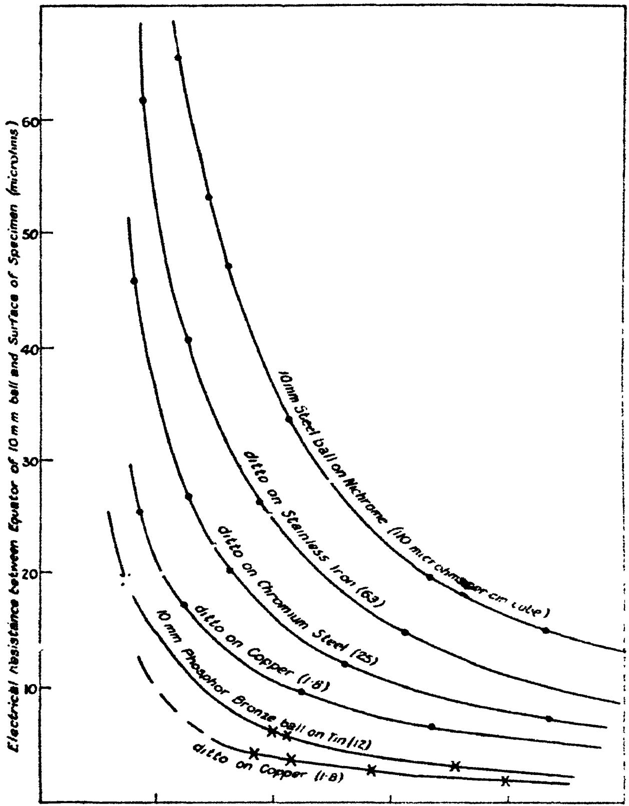
Results obtained on etched surfaces in the above manner are plotted in fig. 2, which shows the measured electrical resistance between the equator of the ball and the surface of the specimen tested, for various-sized impressions, on certain typical materials. (The diameters of the impressions were measured with a travelling microscope in the usual manner.)

The electrical resistances measured are dependent on the diameter of the Brinell impression, on the electrical resistance of the 10-mm. Brinell ball and on the electrical resistance of the material under test. That the last is so will be seen from the specific electrical resistances of the materials tested, which have been written in against each curve in fig. 2.

The two lowest curves in fig. 2 show the results of similar tests on tin and copper, using a 10-mm. phosphor-bronze ball. The electrical resistance of the phosphor-bronze ball, viz., 9 microhms per cm. cube, was considerably lower than that of the hardened steel ball, and consequently the curve showing tests with the phosphor-bronze ball on copper is considerably lower than that for the steel ball on copper. Tests were made which showed that the exact position of the P.D. contact on the surface of the specimen had no measurable effect on the P.D. measured. Tests were made with currents of less than 1 ampere and with currents of over 15 amperes passing through the same small impression (1 to 2 mm. diameter), but any alteration in the resistance results obtained consequent on heating or thermoelectric effects was so small as to be within the limits of experimental error.

Similarly, the hardness of the specimen tested had no measurable influence on the results obtained, since the Brinell numbers (10 mm./3000 kg./30 sec.) of the specimens shown in fig. 2 were as follows: cold-hammered copper 90, chromium steel 190, stainless iron 400, nichrome 200. Furthermore,

Fig. 2.



Electrical resistance between equator of 10-mm. ball and surface of specimen. Plotted against diameter of impression on materials of different electrical resistances.

a test made on tin 4 fell into line, according to the electrical resistance of tin, between the results plotted in fig. 2 for copper and chromium steel.

If the results of fig. 2 are plotted logarithmically, they fall on straight lines according to the following equation (which does not, however, hold for large-diameter impressions):

$$\log \text{E.R.} = \log a + n \log d,$$

$$\therefore \text{E.R.} = ad^n,$$

where E.R. = electrical resistance between equator of 10-mm. ball and surface of specimen; d = diameter of impression produced; and a and n are two constants, each depending in value on the electrical resistance of the material tested plus that of the 10 mm.-ball. The equation is similar in form to Meyer's formula, showing the relationship between the load applied and diameter of impression produced in the Brinell test.

Electrical Resistance Results, using 90° *Cones.*

Results were obtained in a similar manner, using a 90° steel cone, as shown in fig. 1 *b*, instead of a 10-mm. ball. The top drop of potential contact (equivalent to H in fig. 1) was soldered on to the shoulder of the 90° cone. If the electrical resistances measured are plotted against the reciprocals of the diameters of the impressions produced, as has been done in fig. 3 *a*, a linear relationship is obtained for each material, and, as before, the results are dependent on the specific electrical resistance of the material under test. The specific electrical resistances of the materials under test are written in against the appropriate lines in figs. 3 *a* and 3 *b*. Fig. 3 *b* shows similar tests, using a 90° copper cone instead of a steel cone. It will be noted that only soft materials (*e. g.*, tin and lead and their alloys, the latter being specially made for the present purpose) could be tested with the relatively soft copper cone.

It will be seen in figs. 3 *a* and 3 *b* that the lines meet at a point corresponding with zero electrical resistance and a diameter of impression equal to about 50 mm. This is approximately the diameter of impression that would have been obtained if it had been possible to immerse the 90° cone up to the top drop of potential contact, which was 3 mm. or 4 mm. up from the shoulder on the 25-mm. diameter cylindrical part.

It will also be seen that the resistances obtained with the copper cone in fig. 3 *b* are in all cases lower, for equal diameter impressions, than those obtained with the hardened steel cone (fig. 3 *a*) on the same materials. The difference is due—as before—to the lower electrical resistance of the copper cone. The results in figs. 3 *a* and 3 *b* are compared in fig. 4, where the electrical resistances measured for 1 mm.

Fig. 3 *a*.

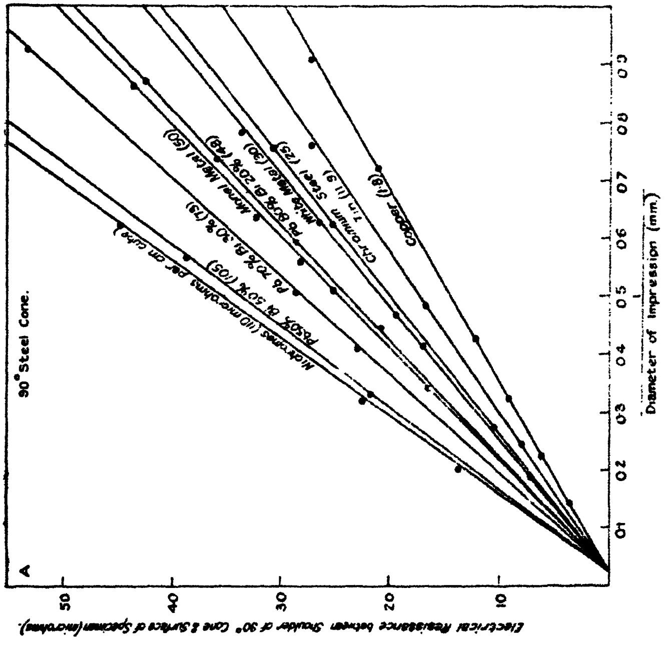
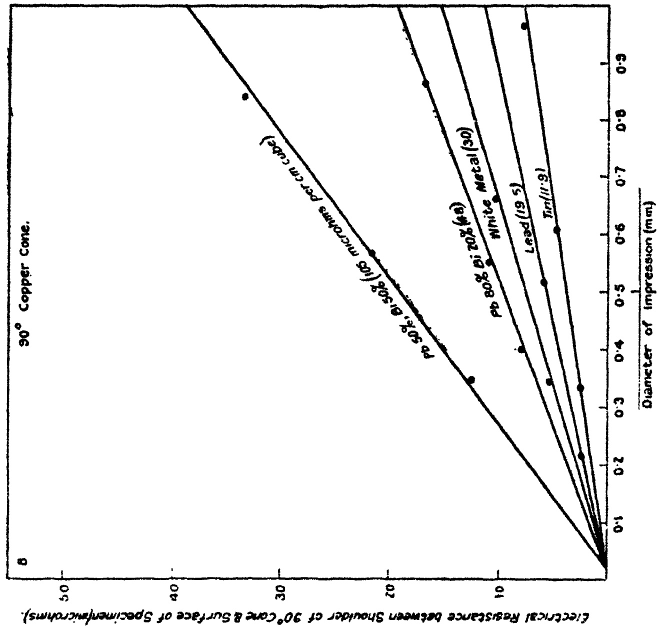


Fig. 3 *b*.

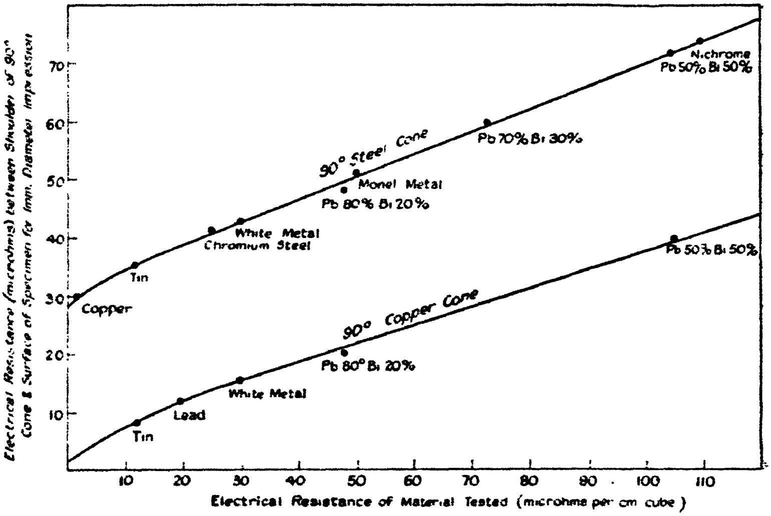


Electrical resistance between shoulder of 90° cone and surface of specimen. Plotted against $\frac{1}{\text{diameter of impression}}$ for various-sized impressions on various materials, using in Fig. 3 *a* a 90° steel cone and in Fig. 3 *b* a 90° copper cone.

diameter impressions on various materials have been plotted against the specific electrical resistances of the materials. This figure shows that the results are directly dependent on the specific electrical resistance of the material under test and on the specific electric resistance of the material used in the 90° cone.

In view of the exact dependence of the results on the specific electrical resistance of the material under test, it is possible to use the method to measure this property of alloys. The method has certain advantages, since it can be applied to pieces of any shape or size without any machining other than filling a flat surface about 5 mm. by 5 mm. or larger.

Fig. 4.



Electrical resistances (microhms) in 90° cone circuit for 1-mm. diameter impressions on various materials plotted against the electrical resistances of the materials tested.

As an instance—the specific electric resistances of 60/40 brass and phosphor-bronze 10-mm. balls were measured by the above method by filling small flat surfaces on them and testing them, as above, with a 90° steel cone and interpreting the results obtained in terms of figs. 3 *a* and 4.

In conclusion the author wishes to thank Principal C. A. Edwards, D.Sc., for facilities for carrying out the present work in his department at Swansea and for his encouragement and interest, and Dr. L. B. Pfeil for drawing fig. 1 and for many helpful suggestions.

LXXIX. *On the Separation of Thorium from Uranium by means of Ether.* By PAUL MISCIATTELLI, *D.Phil.* (*lately Ramsay Memorial Fellow, University of Oxford*)[*].

THE method of separating uranium from thorium by extracting the nitrates with ether has been the subject of divergent results, some workers finding that it is useless in presence of thorium, which is also extracted by the ether, and others that the separation is effective if the salts are well dried and the ether pure and anhydrous. The present research was undertaken to throw light on this question. It deals with the ternary system—$UO_2(NO_3)_2$, $Th(NO_3)_4$, ether—in absence of water. The results for the quaternary system, including water, will form the subject of a separate communication.

The matter is of considerable interest on account of the isotopy of thorium and uranium X. Uranium X was discovered in 1900 by Sir William Crookes[†] by dissolving crystallized uranyl nitrate in ether, whereby the uranium dissolved in the ethereal layer is entirely free from uranium X, and the latter is wholly contained in that part of the uranium dissolved in the aqueous layer formed by the water of crystallization. The extremely sharp and certain separation of what, chemically, is an infinitesimal trace of thorium from uranium by this method in presence of water is very notable. In 1908 Boltwood[‡], for the analysis of many minerals containing uranium and thorium, including thorianite, in which the latter element predominates, successfully used the ether method, extracting the bulk of the uranium from the dried nitrates with anhydrous ether, leaving the thorium nitrate undissolved. But Soddy and Pirret[§] found the method perfectly useless for thorianite, and stated that the ether extract contained more thorium than uranium. Mlle Gleditsch[‖], on the contrary, used the method with success, and stated that she had never observed that the thorium dissolved in the ether if the salts were well dried and the ether pure and dry. The discrepancy was examined by Fleck[¶], who stated that the separation, both when anhydrous and in presence of water, is only complete when small quantities—less than 10 per cent.—of thorium are present. In a mixture containing equal quantities of each salt considerable quantities of thorium dissolved in the ether. He used uranium X as an indicator of thorium, and extracted an aqueous solution, proving that the above separation of Crookes fails if thorium is added in sufficient quantity.

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[*] Communicated by Prof. F. Soddy, F.R.S.

[†] Sir William Crookes, Proc. Roy. Soc. lxvi. p. 409 (1900).

[‡] B. Boltwood, Am. J. Sci. xxv. p. 269 (1908).

[§] F. Soddy and Miss Ruth Pirret, Phil. Mag. [6] xx. p. 345 (1910).

[‖] Mlle Gleditsch, *Le Radium*, viii. p. 256 (1911).

[¶] A. Fleck, Trans. Chem. Soc. ciiii. p. 384 (1913).

In order to throw light upon these apparent contradictions, the ternary system has been systematically examined and the solubility at different temperatures of the anhydrous thorium and uranyl nitrates in anhydrous ether found in presence of one or other, or of both the solid phases. The results are represented in the usual manner by triangular diagrams.

The solubilities were determined by shaking the solutions in presence of excess of one or both solid salts in a large test-tube placed in a Dewar vessel containing melting ice, or in a thermostat at the required temperature. Portions of the solution and of the wet solid were weighed in weighing bottles and separately analysed.

The ether was removed by distillation after the addition of water, to prevent explosions. The cold nearly neutral solution was precipitated by a boiling oxalic acid solution added drop by drop, avoiding an excess that might interfere with the subsequent precipitation of the uranium. The thorium oxalate was ignited and weighed as oxide in the usual manner. The uranium was precipitated from the filtrate by ammonia as ammonium uranate and ignited to constant weight and weighed as U_3O_8. The filtrate was evaporated to dryness, and any uranium, not precipitated in the first precipitation, recovered and added to the main quantity. From the results the weights of the anhydrous nitrates in the mixtures were calculated, that of the ether being determined by difference.

The results for the solubilities at 0° are shown in Table I. and reproduced in the diagram (fig. 1). The first three columns show the percentages of the three components in the saturated solution, the next three the percentages in the wet residue, and the last column the nature of the solid phase in contact with the solution.

These results show that the solubility of uranyl nitrate in anhydrous ether is increased by the addition of thorium nitrate from 22 to 24 per cent. at 0°. The solution saturated with respect to both salts contains 24 per cent. of the former and 3·4 per cent. of the latter. So that under these conditions the method would fail as a means of separating uranium and thorium for analysis.

A series of measurements were next done to see how the composition of the solution saturated with respect to both salts varied with temperature. The results are given in Table II. and are also shown in the diagram (fig. 1).

Fig. 1.

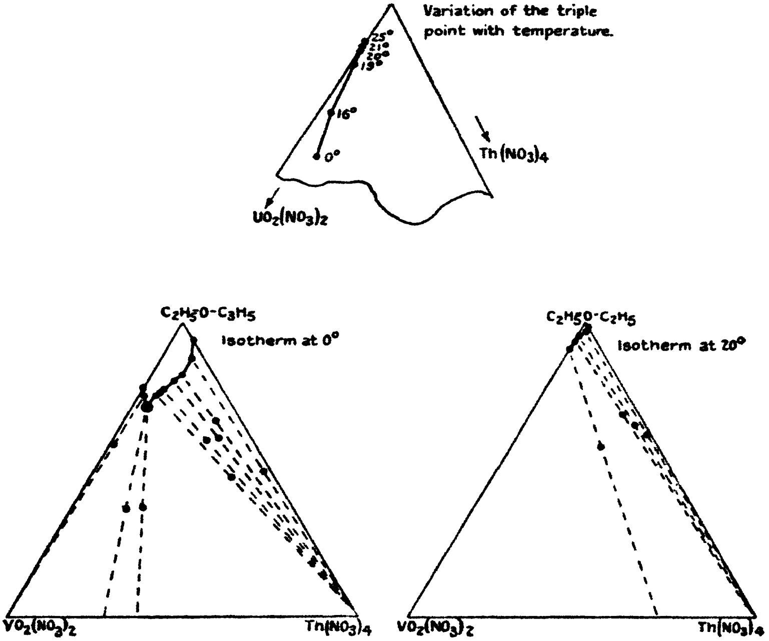

TABLE I. (Temperature 0°.)

$UO_2(NO_3)_2$.	$Th(NO_3)_4$.	Ether.	$UO_2(NO_3)_2$.	$Th(NO_3)_4$.	Ether.	Solid Phase.
22	0	78	—	—	—	$UO_2(NO_3)_2$.
22·5	1·02	76·48	40·1	0·52	59·38	$UO_2(NO_3)_2$
24	3·5	72·57	48·3	15·6	36·1	Both.
24	3·43	72·50	43	20	37	Both.
19·2	4·5	76·3	12	40	48	$Th(NO_3)_4$
18	5	77	—	—	—	„
16·5	5·6	77·9	13	27	60	„
12·2	7	81	9	30	61	„
8·2	8·3	82·5	7	26	67	„
3	8	89	1·8	48·5	39	„
0	5·8	94·2	—	—	—	„

TABLE II.

	$UO_2(NO_3)_2$.	$Th(NO_3)_4$.	Ether.	$UO_2(NO_3)_2$.	$Th(NO_3)_4$.	Ether.
0°	24	3·43	72·57	48·3	15·6	36·1
16°	17·7	1·7	80·6	28·2	20·4	51·4
19°	10·5	0·4	89·1	39·2	15	46·8
20°	8·78	—	91·22	15·5	26	58·5
22°	8	—	92	13·2	23	63·8
25°	7·37	—	92·63	12·2	30	57·8

It will be seen that the solubility in anhydrous ether of both salts, in presence of excess of both, falls markedly with the temperature, and that above 20° thorium nitrate is no longer soluble in a saturated solution of uranyl nitrate. At this temperature and above, the triple point falls on the side of the triangular diagram. Hence it follows that in order to secure a complete separation of uranium from thorium by means of anhydrous ether, the temperature must not be less than 20° and the uranium salt must be in sufficient excess to saturate the solution at that temperature.

Finally, it was thought useful to determine the isotherm for 20°. The results are shown in Table III. and also in the diagram (fig. 1).

TABLE III. (Temperature 20°.)

$UO_2(NO_3)_2$.	$Th(NO_3)_4$.	Ether.	$UO_2(NO_3)_2$.	$Th(NO_3)_4$	Ether.	Solid Phase.
8·78	—	91·22	15·5	26	58·5	Both.
5·5	0·5	94	4·1	27	68·9	$Th(NO_3)_4$
3·1	1	95·9	2·1	32·2	65·7	,,
—	1·4	98·6	—	—	—	,,
—	1·6	98·4	—	—	—	,,

It will be seen that at this temperature anhydrous thorium nitrate is soluble to the extent of 1·5 per cent. in anhydrous ether, and that the solubility diminishes to zero as the quantity of uranyl nitrate increases up to saturation, which is reached at 8·8 per cent.

Summary.

To throw light on the divergent results obtained in the use of ether for the analytical separation of uranium and thorium, the anhydrous ternary system—uranyl nitrate, thorium nitrate, ether—has been examined, and it has been shown that the conditions for the thorium not to be

dissolved are that the temperature must be above 20° and the uranyl salt sufficient to saturate the ethereal solution.

My thanks are due to Professor Soddy for suggesting the work, and to Professor Parravano for his advice in carrying it out.

University of Rome.

LXXX. *On the Thermal Expansions of Mercury and Vitreous Silica. By* F. J. Harlow, *B.Sc., A.R.C.Sc., F.Inst.P., D.I.C.*[*]

Introduction.

THE importance in Thermometry of Precision of an accurate knowledge of the thermal expansion of mercury over as wide a range of temperature as possible is so well known that the appearance of a further publication on this subject embodying the most recent information calls for no excuse.

Since the publication by the author in 1914 (Proc. Phys. Soc. London, Feb. 1914) of the results of measurements of the thermal expansion of mercury contained in an envelope of vitreous silica, measurements of the absolute expansion of mercury for the range 0° to 100° C. have been made by Chappuis (*Trav. et Mém. Int. Bur. des Poids et Mes.* 1917), using the Callendar-Regnault method with several modifications introduced to eliminate certain errors which it was considered might be present in the determinations carried out by Callendar and Moss (Phil. Trans. A, vol. ccxi. Jan. 1911). The results obtained by Chappuis are in much closer agreement with the values published by the author and with Chappuis's values previously obtained by his weight thermometer of "verre dur" than are those obtained by Callendar and Moss, as reference to the values of the coefficients of expansion quoted in Table I. show.

Further, since 1914 additional observations have been made by several observers of the thermal expansion of vitreous silica which make it possible to deduce with greater precision the real expansion of mercury from the author's values of the apparent expansion. The final results, shown in column 5 of Table I., are in closer agreement with those of Chappuis than are those published by the author in 1914 and shown in column 3 of the same table.

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[*] Communicated by the Author.

In the present paper the most probable values of the thermal expansion of both vitreous silica and mercury are considered over the range of temperature 0° to 300° C., and in each case the results are expressed in the form of suitable equations. In addition, tables are constructed from which the volume of 1 c.c. of mercury at 0° C. may be readily obtained at other temperatures throughout the range 0° to 300° C.

TABLE I.

Coefficients of Expansion of Mercury multiplied by 10^8.

Temp. Range.	1. Chappuis' Wt. Therm., 1907.	2. Callendar & Moss's absolute method, 1911.	3. Harlow's Silica Wt. Therm., 1914.	4. Chappuis' absolute method, 1917.	5. Harlow's Silica Wt. Therm., present paper.
0–30°......	18171	18095	18168	18189	18175
0–50°......	18183	18124	18188	18206	18192
0–75°......	18211	18163	18213	18227	18216
0–100° ...	18254	18205	18244	18248	18247

The Thermal Expansion of Vitreous Silica.

Range 0° *to* 100° C.

In the range 0° to 100° C. the available measurements of the thermal expansion of clear vitreous silica are as follows:—

(*a*) Chappuis (*Procès-Verbeaux. Com. Inter. des Poids. et Mes.* 1903). Cylindrical specimen by comparison with a platinum-iridium tripod. Range 0° to 83° C. Linear coefficient:

$$S_0^t \times 10^8 = 38{\cdot}5 + 0{\cdot}115\,t.$$

(*b*) Scheel (*Verh. d. Deutsch. Phys. Gesell.* v. 1903). Cylindrical specimen by comparison with a quartz crystal ring. Range 15° to 100° C. Linear coefficient:

$$S_0^t \times 10^8 = 32{\cdot}2 + 0{\cdot}147\,t.$$

(*c*) Scheel (*Verh. d. Deutsch. Phys. Gesell.* ix. 1907). Ring specimens by absolute method. Range 0° to 100° C.

Linear coefficients :

(i.) $S_0^t \times 10^8 = 21{\cdot}7 + 0{\cdot}2379\,t$.

(ii.) $S_0^t \times 10^8 = 38{\cdot}8 + 0{\cdot}1682\,t - 0{\cdot}000504\,t^2$.

(*d*) Donaldson (Proc. Phys. Soc. Lond. xxiv. 1912). Metre rod by comparison with (i.) invar metre, (ii.) nickel metre, (iii.) 43 per cent. nickel steel metre. Range 0° to 30° C.

Mean equation for linear coefficient:

$$S_0^t \times 10^8 = 38 + 0{\cdot}11\,t.$$

(*e*) Callendar and Eagle (see author's paper, *loc. cit.* 1914).

Linear coefficient :

$$S_0^t \times 10^8 = 78{\cdot}0 - \frac{8650}{t + 175}.$$

(*f*) Scheel and Heuse (*Verh. d. Deutsch. Phys. Gesell.* xvi. 1914). Range 16° to 100° C.

Linear coefficient :

$$S_0^t \times 10^8 = 36{\cdot}2 + 0{\cdot}1813\,t - {\cdot}000340\,t^2.$$

(*g*) Souder and Hidnert (Scientific Papers, Bureau of Standards, no. 529, vol. xxi. 1926). Rods of silica 30 cm. long.

Linear coefficient :

$$S_{20}^{60} \times 10^8 = 40. \quad S_{20}^{100} \times 10^8 = 45.$$

The values of the linear coefficient of expansion calculated from the above formulæ for ranges of temperature employed by the author in his experiments on the thermal expansion of mercury are shown in Table II. Souder and Hidnert's values were reduced to the ranges 0° to t° C. from their results for the ranges 20° to t° C. by plotting, assuming a linear variation with temperature of the coefficient between 0° and 100° C.

There is a very fair measure of agreement among the results obtained by the various authors, and it is considered that the average values given in the last column of Table II. can be applied with considerable precision to the author's measurements of the apparent expansion of mercury for the purpose of evaluating the real expansion.

TABLE II.

Linear Coefficients of Expansion of Silica multiplied by 10^8.

Temperature Range.	1. Chappuis, 1903.	2. Scheel, 1903.	3. Scheel, 1907. (i.)	4. Scheel, 1907. (ii.)	5. Donaldson, 1912.	6. Callendar & Eagle, 1912.	7. Scheel & Heuse, 1914.	8. Souder & Hidnert, 1926.	Average Values.
0–30° C. ...	42·0	36·6	28·8	43·4	41·3	35·8	41·3	34·8	38·0
0–50° C. ...	44·3	39·6	33·6	45·9	43·5*	39·6	44·4	37·1	41·0
0–75° C. ...	47·1	43·2	39·5	48·6	46·4*	43·4	47·9	40·1	44·5
0–100° C....	50·0*	46·9	45·5	50·6	49·0*	46·6	50·9	43·0	47·8

* Extrapolated.

Range 100° *to* 300° C.

For temperatures above 100° C. the most reliable observations are the following:—

(*a*) Randall (Phys. Rev. xxx. 1910). Randall carried out a series of measurements with a clear fused quartz ring over the range 16° to 1100° C., employing the Fizeau method *in vacuo*. The measurements appear to have been carried out with very great care. By means of the average value of the coefficient from 0° to 16° C., viz.

$$S_0^{16}=37\cdot1\times10^{-8},$$

obtained as in Table II. from the results of the observers named therein, Randall's results have been reduced to ranges extending from 0° C., yielding the following values:—

$$S_0^{80}=41\cdot4\times10^{-8},$$
$$S_0^{220}=51\cdot3\times10^{-8},$$
$$S_0^{300}=53\cdot5\times10^{-8}.$$

(*b*) Callendar and Eagle in 1912 (see author's paper, *loc. cit.* 1914). The expansion of a fused silica rod was measured by an interference method, and the results for the linear expansion are represented by the formula:

$$S_0{}^t\times10^8=78\cdot0-\frac{8650}{t+175}.$$

(*c*) Scheel (*Zeits. f. Physik*, v. 1921). Scheel, employing the Fizeau method, made measurements of the expension of a fused quartz ring over the range 16° to 500° C. His results for the linear expansion are represented by the formula:

$$S_0{}^t\times10^8=39\cdot5+0\cdot1282\,t-0\cdot0001698\,t^2.$$

(*d*) Souder and Hidnert (*loc. cit.* 1926). These authors employed the comparator method and carried out observations with specimens 30 cm. long over wide ranges of temperature, which include observations for the range 20° to 300° C. Five different samples of transparent silica were used. Although the values obtained in different tests and with different specimens show rather large variations, yet it is considered that the final average result is entitled to some weight on account of the large number of tests made and the use of five different transparent specimens. The final results for the linear coefficients of expansion for the ranges indicated are as follows :—

$$S_{20}^{100^\circ}\times 10^8=45,\quad S_{20}^{200^\circ}\times 10^8=48,\quad S_{20}^{300^\circ}\times 10^8=52.$$

These, when reduced to ranges from 0° C. by plotting, become

$$S_{0}^{100^\circ}\times 10^8=43,\quad S_{0}^{200^\circ}\times 10^8=47,\quad S_{0}^{300^\circ}\times 10^8=51.$$

A summary of the values of the coefficients of linear expansion of vitreous silica obtained in the above four researches, together with the final average values for the various ranges, are shown in Table III.

TABLE III.

Linear Coefficients of Expansion of Silica multiplied by 10^8.

Temp. Range.	Randall, 1910.	Callendar & Eagle, 1912.	Scheel, 1921.	Souder & Hidnert, 1926.	Average Values.
0–100° C.	43·5	46·6	51·0	43·0	47·6*
0–200° C.	51·0	55·0	58·3	6·7	52·8
0–300° C.	53·5	59·8	62·7	50·9	56·7

* Average of all values, Tables II. and III.

The values for various temperatures over the range 0° to 300° C. of the average values of the linear coefficient of expansion are shown in fig. 1. These values are well represented within the limits of variation of the experimental results by the formula :

$$S_0^t\times 10^8=66{\cdot}3-\frac{3879}{t+103}.$$

The coefficient of cubical expansion, taken as three times the linear coefficient for the reasons given in the author's earlier paper (*loc. cit.* 1914) are represented by the formula:

$$S_0^t\times 10^8=198{\cdot}9-\frac{11637}{t+103}.$$

This type of formula is preferable to a cubic equation of the ordinary type, as it lends itself much more readily to the calculation of the value for any particular temperature range.

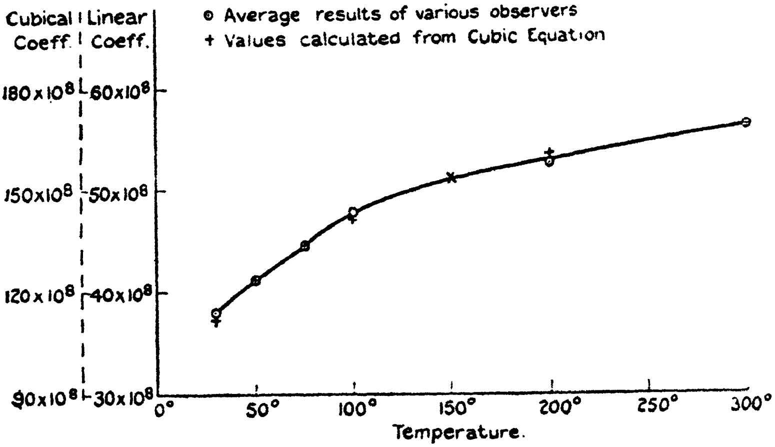
The following quartic equation which represents the variation in volume of an isotropic vitreous silica bulb over the range 0° to 300° C. may, however, be convenient for some purposes :—

$$\frac{V_t}{V_0}=1+10^{-8}\{93{\cdot}6t+0{\cdot}7776t^2-0{\cdot}003315t^3+0{\cdot}000005244t^4\}$$

The Thermal Expansion of Mercury.

From the curve representing the cubical expansion of vitreous silica the quantities to be added to the author's values of the apparent coefficient of expansion of mercury have been calculated, and are set out together with the derived values of the real coefficients of expansion of mercury in Table IV.

Fig. 1.



In Table V. are collected the results obtained by various observers for the real coefficient of expansion of mercury together with the values derived from various formulæ which have been selected to represent the results.

The close agreement at the lower temperatures between the results obtained under such widely different conditions as those quoted in columns 2, 3, and 4 justifies their acceptance as a very close approximation to the true values. These results were obtained with (*a*) The vitreous silica weight thermometer by the author (1914).

(*b*) The weight thermometer of "verre dur" by Chappuis (1907).

(*c*) The absolute method by Chappuis (1917).

They all differ somewhat from the results shown in column 1 of Callendar and Moss, obtained by the absolute method. For the higher ranges of temperature the agreement between the results obtained with the silica weight thermometer (column 2), and those of Callendar and Moss (column 1) is sufficiently close for their mean to be accepted as a close approximation to the true values.

Table IV.

Temp. range.	Volume Coeff. of Expansion of Vitreous Silica, $\times 10^8$.	$\frac{M+m}{M}$.	$\frac{M+m}{M} \times S_0$ $\times 10^8$.	Apparent Coeff. of Expansion of Mercury, $\times 10^8$.	Real Coeff. of Expansion of Mercury, $\times 10^8$.
0–30° C.	114·0	1·005	115	18060	18175
0–50° C.	123·0	1·009	124	18068	18192
0–75° C.	133·5	1·014	135	18081	18216
0–100° C.	142·8	1·018	145	18102	18247
0–140° C.	150·9	1·024	155	18150	18305
0–184° C.	156·6	1·032	162	18220	18382
0–200° C.	158·4	1·035	164	18248	18412
0–250° C.	163·8	1·044	171	18356	18527
0–300° C.	170·1	1·052	179	18489	18668

Representation of Thermal Expansion of Mercury by Formulæ.

In column 5 of Table V. are shown values of the coefficient of expansion which for the ranges 0° to 30° C. and 0° to 100° C. are the average values of those tabulated in columns 2, 3, 4. The values for the ranges 0° C. to 200° C. and 0° C. to 300° C. are the mean values of those tabulated in columns 1 and 2. The form of equation which represents best the experimental results for the variation in volume over the whole range of temperature from 0° to 300° C. is a quartic equation. The following quartic equation has been

TABLE V.

Temperature Range.	1. Callendar & Moss's absolute measurements, ×10⁸.	2. Harlow's Wt. Therm. of Vitreous Silica, ×10⁸.	3. Chappuis' Wt. Therm. of "verre dur," ×10⁸.	4. Chappuis' absolute measurements, ×10⁸.	5. Values used for deriv. of equations, ×10⁸.	6. Values calc. from Quartic (Harlow), ×10⁸.	7. Values calc. from Quartic (Sears), ×10⁸.	8. Values calc. from Cubic (Harlow), ×10⁸.
0–30° C. ……	18095	18175	18171	18189	18178	18178	18174	18170
0–50° C. ……	18124	18192	18183	18206	—	18196	18194	18192
0–75° C. ……	18163	18216	18211	18227	—	18221	18221	18219
0–100° C. ……	18205	18247	18254	18248	18250	18250	18251	18250
0–140° C. ……	18280	18305	—	—	—	18304	18306	18306
0–184° C. ……	18371	18382	—	—	—	18378	18379	18379
0–200° C. ……	18406	18412	—	—	18409	18409	18410	18409
0–250° C. ……	18525	18527	—	—	—	18522	18522	18520
0–300° C. ……	18657	18662	—	—	18663	18663	18663	18663

calculated by making use of the values of expansion coefficients shown in column 5:—

$$\frac{V_t}{V_0}=1+10^{-8}\{18153{\cdot}8\,t+0{\cdot}7548\,t^2+0{\cdot}001533\,t^3+0{\cdot}00000536\,t^4\}.$$

The values of the expansion coefficients calculated from this equation for the various ranges employed in the author's experiments are given in column 6. Their close agreement with the values obtained experimentally as set out in column 2 will be observed.

In the discussion of the author's earlier paper, Mr. Sears, of the National Physical Laboratory, gave the following quartic equation, which he derived on certain assumptions from the experimental results then available, viz.:—

$$\frac{V_t}{V_0}=1+10^{-8}\{18145{\cdot}6\,t+0{\cdot}9205\,t^2+0{\cdot}0006608\,t^3+0{\cdot}000006732\,t^4\}.$$

The values of the expansion coefficients calculated from this equation are given in column 7 of Table V. It will be seen that a very close agreement exists between the values obtained from the two quartic equations, so that the present investigation may be taken as a verification of the accuracy of the quartic equation given by Sears, full particulars of the derivation of which were published in the discussion on the author's paper of February 1914 (*loc. cit.*).

In order to furnish in the present paper a table of values of the volume of 1 c.c. of mercury at 0° C. when measured at various temperatures over the range 0° to 300° C., it was found to be much more convenient to employ an equation of the type

$$\frac{V_t}{V_0}=1+\left(a+\frac{b}{c-t}\right)t\times10^{-8}.$$

The following values of the constants were calculated from the coefficients of expansion shown in column 5 of Table VI. for the ranges 0° to 100° C., 0° to 200° C., 0° to 300° C., viz.:—

$$a=17559{\cdot}1,$$
$$b=369555,$$
$$c=634{\cdot}7.$$

The equation containing these constants represents the experimental results with considerable accuracy well within the limits of variation of the experimental results shown in columns 2, 3, and 4, particularly for the range of temperature

TABLE VI.

Temp.	Mean Coeff. of Expansion of Mercury, 0° to *t*°.	Volume of 1 c.c. of Mercury at 0° C. measured at temperatures from 0° to 300° C.									
		0°.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.
0.........	·00018154	1·000000	0181	0363	0544	0726	0908	1090	1271	1452	1634
10.........	18161	1816	1998	2180	2362	2544	2725	2907	3089	3270	3452
20.........	18169	3634	3816	3998	4180	4362	4543	4725	4907	5089	5271
30.........	18178	5453	5635	5817	5999	6182	6364	6546	6728	6910	7093
40.........	18187	7275	7457	7639	7821	8003	8186	8368	8550	8733	8915
50.........	18196	9098	9280	9463	9645	9828	$\overline{0010}$	$\overline{0193}$	$\overline{0375}$	$\overline{0558}$	$\overline{0741}$
60.........	18206	1·010924	1106	1289	1472	1654	1837	2020	2202	2385	2568
70.........	18216	2751	2934	3117	3300	3483	3667	3850	4033	4216	4399
80.........	18227	4582	4765	4948	5131	5314	5497	5680	5864	6047	6231
90	18238	6414	6598	6781	6964	7148	7332	7515	7699	7883	8066
100.........	18250	8250	8434	8618	8802	8986	9170	9354	9538	9722	9906
110.........	18263	1·020090	0274	0458	0642	0826	1011	1195	1379	1564	1748
120.........	18277	1933	2117	2302	2486	2671	2855	3040	3225	3409	3594
130.........	18291	3779	3964	4148	4333	4518	4703	4888	5073	5258	5443
140.........	18306	5629	5814	5999	6184	6370	6555	6740	6926	7111	7297
150.........	18322	7482	7668	7854	8039	8225	8411	8597	8782	8968	9154
160.........	18338	9340	9526	9712	9898	$\overline{0085}$	$\overline{0271}$	$\overline{0457}$	$\overline{0643}$	$\overline{0830}$	$\overline{1016}$
170.........	18354	1·031202	1389	1575	1762	1949	2135	2322	2509	2696	2883
180.........	18372	3069	3256	3443	3630	3817	4004	4191	4378	4566	4754
190.........	18390	4941	5129	5316	5504	5692	5879	6067	6254	6442	6630
200.........	18409	6818	7007	7195	7383	7571	7759	7947	8136	8324	8513
210.........	18429	8702	8890	9079	9267	9456	9645	9834	$\overline{0023}$	$\overline{0212}$	$\overline{0401}$
220.........	18450	1·040590	0780	0969	1158	1348	1537	1726	1916	2106	2296
230..... ...	18472	2486	2676	2866	3056	3246	3436	3626	3817	4008	4198
240.........	18496	4389	4580	4770	4961	5152	5343	5534	5725	5917	6108
250.........	18520	6299	6491	6682	6874	7066	7258	7449	7641	7833	8026
260.........	18545	8218	8410	8603	8795	8988	9181	9373	9566	9759	9952
270.........	18572	1·050145	0339	0533	0726	0919	1113	1307	1500	1694	1888
280.........	18602	2083	2278	2472	2666	2860	3055	3250	3445	3640	3835
290.........	18632	4030	4226	4422	4618	4813	5009	5204	5399	5596	5793
300.........	18663	5989	—	—	—	—	—	—	—	—	

100° to 300° C. In column 8 of Table V. are shown the values of the expansion coefficients calculated by means of the corresponding equation, viz. :—

$$\alpha_0^t \times 10^8 = 17559{\cdot}1 + \frac{369555}{634{\cdot}7 - t}.$$

Table of Volumes and Expansion Coefficients.

Table VI. gives the values of the expansion coefficient calculated for the temperature ranges 0° to 10°, 0° to 20°, 0° to 30°, etc , up to 0° to 300° C. It also gives in a manner leading to easy interpolation the volumes occupied by 1 c.c. of mercury at 0° C. when measured at various temperatures in the range 0° to 300° C. The application of the usual proportionate interpolation gives results well within the limits of accuracy of the experimental determinations.

In the compilation of Table VI use was made of the quartic equation for the range 0° to 100° C. and of the cubic equation for the higher ranges up to 300° C., as follows :—

Range 0° *to* 100° C.

$$\frac{V_t}{V_0} = 1 + 10^{-8}\{18153{\cdot}8\,t + 0{\cdot}7548\,t^2 + 0{\cdot}001533\,t^3 + 0{\cdot}00000536\,t^4\}.$$

Range 100° *to* 300° C.

$$\frac{V_t}{V_0} = 1 + \left\{17559{\cdot}1 + \frac{369555}{634{\cdot}7 - t}\right\} t \times 10^{-8}.$$

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LXXXI. *The Application of a Valve Amplifier to the Measurement of X-Ray and Photoelectric Effects. By* J. Brentano, *D.Sc., Lecturer in Physics, Manchester University*[*].

My attention has been directed to a paper by Mr. Wynn-Williams with the above title in the August number of the Philosophical Magazine[†].

I was particularly interested in Mr. Wynn-Williams's results, as the arrangement adopted by him bears close resemblance to an arrangement for measuring ionization currents described by me in 'Nature,' Dec. 22nd, 1921. This was introduced as a more sensitive method to take the place of the method evolved by Malassez for the measurement of X-ray intensities, where greater sensitivity is required, and was demonstrated by some experiments showing the change of ionization along the path of α-rays (Bragg's curves) *.

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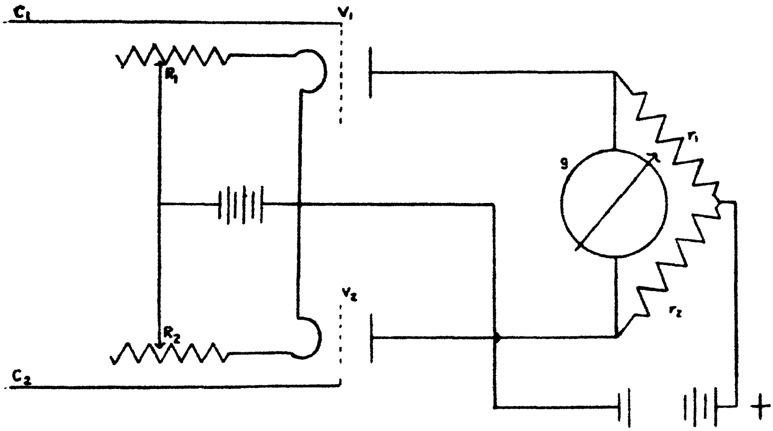
[*] Communicated by the Author.

[†] C. E. Wynn-Williams, Phil. Mag. vi. p. 324 (1928).

Mr. Wynn-Williams does not quote the earlier publication in his present paper, and it will indeed have escaped the attention of most readers, so that it may be recalled with a few words. In order to shorten the discussion, the diagrammatic sketch given in 'Nature' may be referred to again (see fig. 1).

Fig. 1.



The three electrode valves V_1 and V_2 form two arms of a Wheatstone-bridge containing the galvanometer g, the two other arms of which consist of ohmic resistances r_1 and r_2; a common high-tension battery is used for the anode currents of the two valves, and a common battery is also used for supplying the heating currents to the filaments, which are

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* J. Brentano, 'Nature,' cviii. p. 532 (1921).

The comments I wish to make refer to the general method, as the various applications depend on the sensitivity, steadiness, and immunity from external disturbances of the bridge method used. In connexion with my own work I was particularly interested in X-ray measurements when discussing the arrangement in 'Nature.' For the development of a valve amplifier and the study of the particular conditions of photoelectric measurements the work of Meyer, Rosenberg and Tank, *Arch. Sc. Phys. et Nat.* (5) p. 260 (1920) and of Rosenberg, *Zeitschr. f. Phys.* vii. p. 18 (1921) should be considered, which seem not to have been noticed by Mr. Wynn-Williams.

controlled by resistances R_1 and R_2. Any variation of the potential of the grid of one of the valves produces a deflexion of the galvanometer. The purpose of the second valve is to introduce in the two adjacent arms of the bridge elements which can be adjusted so as to present similar characteristics with respect to any variation of the E.M.F.'s acting in the circuit.

It will be seen that this arrangement is practically the same as the arrangement used by Wynn-Williams, except that he controls the ratio of the heating currents of the two filaments by interposing a slide-wire resistance of constant value and a sliding contact instead of the two separate resistances R_1 and R_2. He also acknowledges this similarity in a previous publication, to which reference is made in his present paper, where he describes the arrangement discussed in 'Nature' in general terms, and refers to it as the "old method," emphasizing that the modification introduced by him consists in the slide-wire, which, in conjunction with the discussion given in the paper, is considered to be an improvement of vital importance *.

Comparing the limit of sensitivity obtained by Wynn-Williams, which for current is 10^{-12}–10^{-13} amp. and for voltage $1{\cdot}6 \,.\, 10^{-4}$ volt, with the sensitivity found in my early experiments with valves and instruments not particularly suitable for obtaining the best results, which was $3 \,.\, 10^{-13}$ amp. resp. $1{\cdot}2 \,.\, 10^{-4}$ volt, the improvement introduced by the slide-wire is not apparent, and it seems, indeed, mainly a question of the technical execution whether there is a preference for one or the other way, so that I find it difficult to agree with him on this particular point.

The limits of the sensitivity obtained by Wynn-Williams are actually imposed by the unsteadiness of the arrangement, and the discussion given in his paper shows that some points have not been considered which are essential for the practical operation of the method and which lead to an application which in some respects may appear more efficient. Although desiring to appreciate his work, some criticisms cannot be

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* C. E. Wynn-Williams, Proc. Camb. Phil. Soc. xxiii. p. 811 (1927). *Cp.* fig. 1 *b* and fig. 1 *c* with the figure reproduced from 'Nature.' In discussing the merits of the alteration, it is said (p. 814): "The necessary modification seems at first sight to be so superficial as to render such a claim absurd, it consisting merely of 30 cm. of eureka wire... But a consideration of the theoretical side of the question shows that this is not the case, the inclusion of the slide-wire EF being the most natural and simplest way of enabling certain theoretical conditions to be realized experimentally, and not a haphazard addition to an existing older circuit."

omitted in order to do full justice to the bridge method employed.

In the discussion Wynn-Williams considers a particular way of operation which neglects some of the possibilities for compensating the effect of the inequality of the two valves with respect to variations of the E.M.F.'s acting in the circuits, and which takes no account of the particular features of the modern highly-evacuated valves. Applying the relation of the Wheatstone bridge, the effect of voltage fluctuations in the two battery circuits is considered, giving particular attention to the compensation of fluctuations in the heating circuit*. In doing this he finds it difficult to obtain at the same time compensation of variations in the anode circuit, and no practical way is indicated for carrying this out independently, so that it is suggested to disregard compensation for the latter.

This is probably the reason why, in the earlier experiments of Wynn-Williams, without special shielding external perturbances were greatly felt, so as to induce him to recommend the instrument as a sensitive wireless detector.

Another reason which may contribute to unsteadiness is possibly due to the fact that while connecting one grid to the collecting electrode of the ionization chamber and keeping the other grid insulated, no consideration seems to be given to the capacity connected to each grid. When using the method in this particular way, an essential condition for obtaining steadiness is that the capacities connected with the grids should be of the same order, the exact values depending on the characteristics of the two valves and on the insulation of each grid.

In his recent experiments Wynn-Williams is successful in operating the instrument in the neighbourhood of an X-ray bulb. This is obtained by very careful screening, and can thus scarcely be considered as a test for the intrinsic merits of the method. In fact, it has been shown by Du Prel † that X-ray measurements can be carried out with a valve arrangement with a very high degree of sensitivity, which has no compensating features, when proper shielding precautions are taken.

The point which merits special attention refers to the particular properties of the highly-evacuated valves which are now available. In my early experiments described in

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* A. Marcus, Phys. Rev. xxxi. p. 302 (1928), gives prominence to the same point.

† Du Prel, *Ann. d. Phys.* lxx. p. 199 (1923).

'Nature,' only soft valves were available so that it was impossible to establish a sufficiently dense space-charge in the neighbourhood of the filament. In such conditions the anode current varies greatly with any change in the temperature of the filament, and the control of the heating current is therefore of the greatest importance. Mr. Wynn-Williams concentrates his attention on the same point, whereas the fluctuations of the heating current with highly-evacuated valves have actually comparatively little effect when the valves are used under suitable conditions. It will also be found possible to dispose the heating circuit in such a way as to greatly reduce the effect of electromagnetic disturbances while the anode circuit containing the bridge is much more exposed, and compensation with respect to variations of the E.M.F. acting in this circuit should therefore be considered in the first place. This compensation was only alluded to in my note and has been discussed in a paper read at the Hambourg meeting of the Physical Society last summer.

The main points of the method may be summarized:—

The heating currents of the valves, which are of the low-temperature emitting type and highly evacuated, have such values that the filaments are surrounded by sufficiently dense space-charges.

Referring to the well-known equation:

$$i_a = aV_g + bV_a + c,$$

which may be used to indicate for the purpose of the discussion in approximation the relation between the anode current i_a, the grid voltage V_g, and the anode voltage V_a, the quantities a, b, and c being constants; by differentiating $b = \frac{\partial i_a}{\partial V_a}$. It will thus be seen that in order to establish balance in the bridge and to maintain this for a variation of the E.M.F. in the anode circuit, the double relation

$$i_1 : i_2 = r_2 : r_1$$

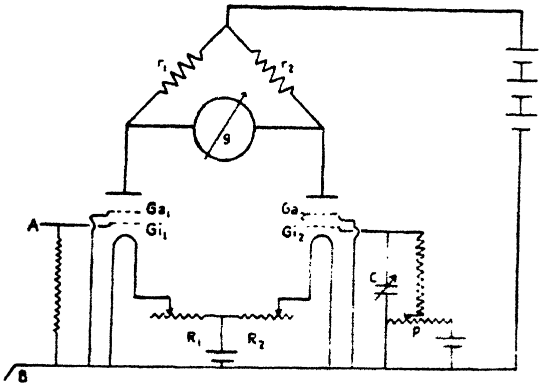
$$\text{and} \qquad b_1 : b_2 = r_2 : r_1$$

must be satisfied, where the indices 1 and 2 refer to the two valves of the bridge. From the second equation a definite ratio is therefore fixed for the resistances r_1 and r_2, and the equilibrium of the bridge has to be determined by giving proper values to the potentials of the grids. If the grid which is used for the measurement of potential differences or which is connected to the ionization chamber is given the potential which corresponds to the state of equilibrium, a definite voltage must be applied to the grid of the other valve by connecting it to a potentiometer with a suitable E.M.F.

In this way a remarkable degree of immunity from external disturbances can be obtained. In one experiment, using purposely two valves of different type with greatly different characteristics for which the ratio $r_1/r_2=1{\cdot}75$ was found to give correct balance, a change of the anode voltage by ± 2 volts produced a deflexion of the galvanometer of 0·3 scale-division; the sensitivity in this particular case was $2\,.\,10^{-11}$ amp./scale-div.

When a high degree of sensitivity is desired, the electrostatic induction between the anode and grid of the valves must be considered. Any variation of the potential of one of the grids is accompanied by a variation of the potential distribution of the anodes, which reacts on the grids; with a grid which is highly insulated or connected to earth through a high resistance a disturbance is thus produced. This effect can be reduced by reducing the resistances r_1 and r_2 (there is, in fact, no advantage when they are much larger than the resistance of the galvanometer), or more effectively by using valves with two grids, the outer grids being connected to earth. The current sensitivity observed with such an arrangement was $4\,.\,10^{-14}$ amp., the voltage sensitivity $2\,.\,10^{-6}$ volt, and the power dissipation for one scale-deflexion $8\,.\,10^{-19}$ watt.

Fig. 2.



The arrangement which corresponds to these conditions is indicated by fig. 2. G_{a_1} and G_{a_2} are the outer grids, G_1

is the inner grid connected to A which can be brought in connexion with the ionization chamber while B leads to earth, G_1, is the inner grid connected to the potentiometer p through a high resistance with a capacity c in parallel, in order to compensate for the capacity effect produced by external fields, which has been mentioned in the earlier part of this note.

The heating circuit was arranged so as to be compact and to present a minimum of "inductive area," and in operation no compensation of the heating circuit was found necessary, but this could easily be effected without interfering with the other compensating conditions if required. The use of double-grid valves is indicated here, as it increases the steadiness of the bridge, but actually the same sensitivity for current and for voltage was found with single grid valves, when the balancing conditions were observed.

It may be mentioned that the necessary variability so as to satisfy the relations imposed by the valve characteristics and to maintain the balance of the bridge with respect to fluctuations of the E.M.F.'s acting in the anode circuit can be obtained by interposing a resistance between one of the anodes and the galvanometer branch. In this way the potentiometer can be dispensed with; the setting is not quite so convenient.

Clarens,
Dec. 28th, 1928.

LXXXII. *On some Regularities in the Table of Elements, and their Cosmological Import.* *By* D. Strömholm [*].

MENDELEJEFF arranged his system of the elements according to their atomic weight, assuming the qualities of the elements to be periodic functions of their atomic weight. This idea proved to work rather well, though there appeared to be a few exceptions, which caused much trouble. Now the state of these matters is totally altered; the elements are arranged according to the atomic numbers, which are found by means of the Röntgen spectra. The atomic number is considered to be determined by the number of electrons in the envelope of the atom; this is determined by the positive charge of the atomic nucleus, which is the excess of positive units over negative ones (electrons) in the nucleus. As the nuclei to a certain number of positive units can contain a varying number of electrons, it follows that one and the same atomic number can belong to different atoms of different atomic weights, but still of identical chemical properties, so called isotopes, the connexion between which is that the difference between positive and negative units in the nuclei is the same. That Mendelejeff's system is not quite exact therefore no longer causes any wonder. But it may be worth while to give some thought to the converse problem of how it is possible that Mendelejeff's system can be applicable to the extent that it actually is. Its approximate validity shows, of course, that the atomic weight of an element, respective the mean value of the atomic weights of its isotopes, is connected with the atomic numbers by some fairly strict rules.

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[*] Communicated by the Author.

The cause of the existence of isotopes being that in the atomic nuclei, together with the positive units of weight 2, there can exist negative units, electrons (of an all but infinitesimal weight), our task is to investigate if the percentage of the electrons in the nuclei is dependent on the atomic weight. For the rest, the common conception seems to be that the positive units themselves contain electrons; thus that they are composed of two positive units of weight 1, cemented together by one electron; but we do not propose to deal with such electrons here. If there existed no electrons in the nuclei, then the atomic number would be equal to half the atomic weight, the weight of a positive unit being 2. Such is, indeed, the case in many elements of a low atomic number up to No. 20 Ca, but in no higher element, and our investigation has thus only to consider the elements of high numbers, beginning with No. 21. Regarding these elements, we form a function for each of them denoting the proportion between positive and negative units in the nucleus. Half the atomic weight is equal to the number of positive units; the difference between this number and the atomic number gives the number of electrons in the nucleus; the quotient between these two quantities, $\frac{\text{at. w.}}{2} : \left(\frac{\text{at. wt.}}{2} - \text{No.}\right)$, gives the proportion between positive and negative units in the nucleus. It is this function that we shall use in the following, indicated posit./negat. We shall first give some examples of the values of posit./negat. No. 21, Sc 14·5; 30, Zn 12·1; 33, As 8·3; 47, Ag 7·7; 51, Sb 6·1; 92, U 4·4. If we write down all these values of posit./negat. in a row according to the atomic numbers, we find the following rules:—Firstly, a certain steadiness in the progress of the row, the very cause of the validity of Mendelejeff's system; further, we find, as the cited examples show, that the values of posit./negat. decrease with the increasing atomic weights, *i. e.*, the higher the atomic weight the higher the percentage of electrons in the nuclei. Lastly, one more peculiarity appears, namely that this decline of the values posit./negat. is not gradual, but proceeds by distinctly pronounced leaps, separated by long stretches where the values are constant. From this point of view the table of the elements can thus be divided into distinct stages; these we shall treat separately. These stages are furthermore given yet more prominence by a special circumstance, that the first element of each stage is remarkably rare.

In the first stage, containing the elements up to No. 20, there exist, as said before, many elements the atomic number of which is equal to half the atomic weight, and which have therefore no electrons in the nuclei. Still another circumstance, found in the investigation of isotopes, is to be mentioned here: if the weight of all positive units were 2, it would result that the atomic weight of all isotopes would be expressed by even numbers; but as many isotopes are known the atomic weight of which is an odd number, there must also exist positive units of an odd weight, certainly 3. As a matter of fact, most cases among elements belonging to the first stage, where the atomic number is less than half the atomic weight, seem to depend on the occurrence of positive units of the weight 3. I think, therefore, that if we say that the ratio posit./negat. in this stage is infinitely great, we express the essential matter, though the rule suffers exceptions.

The second stage comprises Nos. 21–30, from the rare Sc to Zn. The values posit./negat. are: No. 21—Sc 14·5; Ti 12 3; V 10·2; Cr 13·0; Mn 11·2; Fe 14·7; Co 11·8; Ni 21·7; Cu 11·4. No. 30—Zn 12·1. The average of the whole stage is 13·3; of Nos. 21–25 it is 12·2; of Nos. 26–30 it is 14·3 (or, if Ni is excluded, 12·5). Though the values vary rather much, they show thus no tendency at all to decrease at the higher atomic weights, which still holds good if we exclude the very irregular Ni. The stage is thus well marked.

The third stage comprises Nos. 31–47, from the rare Ga and Ge at least to Ag. The values of posit./negat. are: No. 31—Ga 9·0; Ge 8·5; As 8·3; Sc 7·1; Br 8·1; Kr 7·6; Rb 7·4; Sr 7 5; Y 8·1; Zr 8·1; Nb 8·1; Mo 8·0; Ru 7·4;

Rh 7·9 ; Pd 7·2. No. 47—Ag 7·7. The average for the whole stage is 7·8 ; for 31–38 it is 7·9 ; for 39–47 it is 7·8. The stage is thus well marked.

The borders on the next stage are somewhat confused, Nos. 48 and 49 both showing the intermediate value 6·9. As 49 In is very rare, it is probably the first element of stage 4. The range of atomic weights over which the second stage extends may be expressed by the difference in atomic weight between Ca, the last element of stage 1, and Zn, the last one of stage 2, and is thus about 26. The range of stage 3, a little vague, as we have seen, is about 45 ; thus much greater than that of stage 2. It seems thus that a higher stage has a greater range than a lower one ; true, the range of the first stage is greater than that of the second, but it is very possible that the first stage is equivalent to more than one of the following stages, a subject that we shall return to later on. The discerning of stages in the highest part of the system is not so sure. The average of posit./negat. of Nos. 50–60 is 5·85, with the extremes 6·3 and 5·4 ; of Nos. 62–72 it is 5·4 ; of Nos. 73–83 it is 5·0, with the extremes 5·1 and 4·9. Probably two stages, the fourth and the fifth, are to be discerned, the boundary between which lies somewhere among the rare Nos. 61–72. If we apply the rule that the ranges of the stages increase towards the higher part of the system, we ought to place the border as high as possible : thus at 72 Hf the two most stable elements from the radioactive part of the system, Th and U, have both the low ratio posit./negat. $=4·4$; but as these values do not belong to the average of many isotopes, but to single isotopes, which are preserved by the slowness of their radioactive disaggregation, they are not comparable to the other values, and cannot be sufficient to assign the radioactive elements to a stage of their own. Indeed, if stage 5 commences with 72 Hf, then its range may extend beyond the highest known radioactive elements. For the different stages we have thus found the following averages of the values posit./negat :—Stage $1=\infty$; st. $2=13·3$; st. $3=7·8$; st. $4=5·85$; st. $5=5·0$.

The figures on which the mentioned regularities are founded are, of course, not altogether unobjectionable. Some atomic weights are the average of isotopes, whilst other elements are homogeneous, and it may seem questionable if they are altogether comparable ; from Aston's table of isotopes, however, it is evident that in the former cases, as a rule, the weights of the most important isotopes are not very different. The occurrence of isotopes of an odd atomic weight, thus of positive units of weight 3, is certainly a cause of errors. In such cases the atomic weight ought, of course, to be corrected so that the unit 3 was reckoned only to weigh 2; the atomic weight would be diminished by 1. As Aston's table of isotopes is complete up to No. 40, such a correction can be made up to this number; and it is thus easy to verify that the rules stated are not impaired hereby. It might be maintained that it were possible that two units of weight 3 would occur in one atom, which could not be perceived, as the atomic weight would then be even, but would affect our results appreciably. But in the first stage this is impossible in most cases, in consequence of the smallness of the atomic weights. It is moreover obvious that, if there can be discerned any general rule about the occurrence of the units 3, this would prove that their occurrence is ever manifest, never disguised. As a matter of fact, such a rule is to be discerned in Aston's table as valid over the whole range of elements (except the very lowest up to No. 7); the isotopes of an odd atomic weight occur well-nigh exclusively in elements of an odd number, and these are well-nigh exclusively composed of such isotopes.

In consequence of this rule, the corrections mentioned for the occurrence of the units of weight 3 have the effect that the values posit./negat. are raised in all elements of odd numbers, not in the even ones. Regarding stage 2, this amendment renders the values more equable, except that of Sc, which becomes rather high. In the higher stages, however, the uncorrected values are already rather higher in the odd than in the even elements, which circumstance then becomes enhanced by the correction. It seems, then, as if the occurrence of the units 3 would lessen the capacity of the nuclei to absorb electrons: this may seem intelligible, as these units of weight 3 certainly are bigger than the ordinary ones, and therefore encroach upon the room available.

Regarding the lowest stages, it may be of interest to note the absolute number of electrons too. In stage 2, where many of the elements are homogeneous, the nuclei contain mostly two electrons. Only in the highest elements, Cu and Zn, do isotopes with three electrons attain some importance. But, in addition, nuclei with one electron occur in this stage rather irregularly, namely in Sc, in the chief isotope of Ni, and in a subordinate one of Fe. The isotopes of stage 1, which have electrons in the nuclei, contain as a rule one, argon two. The unsteadiness of the values posit. negat. in stage 2 depends partly on so many elements being homogeneous, but most on the irregular occurrence of atoms with one electron.

The rules that we consider here are thus:—(1) The percentage of electrons in the nuclei is zero in the elements of low atomic weights; it commences to be evident at No. 21, and increases then with increasing atomic weights: (2) this increase is not gradual, but proceeds in distinctly marked stages.

These rules seem apt to give occasion to theoretical speculations, and the basis of these can only be hypotheses about the genesis of the elements, at least the heavier ones. Such a notion has been rendered somewhat familiar by the discovery of the radioactive transmutations, which show that the elements are not essentially unalterable. At least the radioactive elements, being perishable, must have been created; true, the fundamental elements, U and Th, have very long periods, and by assuming great original stores of them, the commencement of things would be placed at a distance, though not infinitely, at least excessively great; but as the stable ultimate products of the radioactive reactions exist only in insignificant quantities, such an assumption is not admissible. The radioactive reactions of disintegration proceed under an extremely great development of energy; the radioactive elements are thus strongly endothermical. It is then a rather necessary conclusion by analogy that the elements of high atomic weights are altogether endothermical, though it is uncertain how far down in the series this holds good. The only locality where the creation of elements can be supposed to take place is the interior of the earth and other celestial bodies; the huge concentration of energy by heat and pressure that must be assumed to prevail there makes it acceptable as the birthplace of formations very rich in energy.

That most elements seem to be totally unalterable is no essential hindrance, as it is very common that reactions which do not take place at lower temperatures come to pass at higher ones. The radioactive reactions, however, though showing that the elements are not essentially unalterable, have given a hard check to speculation; the speed of these reactions has proved to be independent of the temperature, which is totally different from the laws of ordinary chemical reactions, and seems to make it dubious if experience from the latter is to be applied at all to element-shaping reactions. But still it seems inadmissible to assume an altogether essential difference between these two classes of reactions, and it does not seem impossible to guess in which direction an explanation of the puzzling insensibility of element-reactions to temperature is to be sought for. Other paradoxes from the province of the science of heat are known which are explained thus: that the expected exchange of energy is prevented, by some cause or other, from being realized; for instance, in the Leiden frost phenomena it is the question of a screen of gases. Now the atoms are supposed to consist of a nucleus, the seat of the radioactive reactions, surrounded by a swarm of electrons; it may be this, principally its outermost layer, that prevents the energy from without from attaining to the nucleus. But in the interior of the earth, not only may the temperature be very high, but the electron envelope is exposed to an enormous pressure which prevents its movements, and thus prevents it from appropriating the energy, which then may penetrate to the nucleus. It seems admissible to assume that in the interior of the earth element-shaping reactions take place, though probably slowly, certainly resulting in equilibria the components of which are elements.

The main features of the conditions of these equilibria ought to be as follows:—The effect of high temperature is that endothermic elements are favoured, according to our assumption elements of high atomic weight. The pressure tends to diminish the volume. As the volume mainly depends on the electron envelope, this is compressed in the first place; but to this it opposes an extraordinary resistance; therefore also element-reactions, diminishing the volume, may attain importance. Such an one is certainly the increase of the atomic weights; thus the collection of matter in greater heaps. Ordinarily the specific gravity is great when the atomic weight is high; and by comparison of homologous elements we find, indeed, the specific gravity regularly increasing with the atomic weight. We find it thus probable that high temperature and high pressure work in the same direction, increasing the atomic weights. Further, as it is mainly the electron envelope that determines the volume, the removal of electrons must cause reduction of the volume, and thus be an effect of pressure; such a removal is effected by the absorption of electrons into the nuclei. We have seen, indeed, that the greater the atomic weight is, the greater is the percentage of electrons in the nuclei; it is therefore logical to assume that it is one and the same cause that makes the mass of the nucleus and its percentage of electrons increase. This common cause is the pressure that prevailed in the *milieu* where the element was created.

The percentage of electrons in the nuclei would thus give us a direct measure of the pressure prevailing at the place where the element arose. The first elements up to No. 20

would therefore not require a very high pressure for their creation, whilst this is the case in all elements of higher numbers, the higher the atomic weight the greater must the pressure be, and the greater therefore is the depth from which the element came. Furthermore, we have found that the increase of the percentage of electrons with the atomic weight is not gradual, but proceeds by leaps and is divided in several stages. This circumstance is, from our standpoint, only to be explained thus: that the interior of the earth, the birthplace of these elements, is not one homogeneous space where all transitions between elements are gradual and continuous, but is composed of several layers, each of them being a homogeneous space where all elements that belong to one of the stages mentioned above are created; elements of higher or lower atomic weights are perhaps not altogether missing, but very disfavoured in the existing equilibrium. Within such a layer comes a new one with a new, limited set of elements, and so on.

A thermodynamic explanation may be given to this conception. We know that the separation of positive units (as α-particles) from radioactive elements is a strongly exothermic process: then the inverse reaction must be endothermic, and we assume something of the kind to be valid in a great part of the element system. If we could build up the elements by affixing one positive unit after the other, we should then find these synthetic reactions endothermic, and this would hold good, at least from No. 21. But the heat absorbed would not in all cases have such, we may say, fantastic measures as are shown in the radioactive reactions; it is probably low in the lower parts of the element system, and increases with increasing atomic weights. This increase is not gradual, but proceeds by bounds: the quantity of heat absorbed at the affixing of one positive unit remains tolerably constant over a certain range; then it suddenly rises to a higher, probably a much higher, value, which then remains fairly constant over a new range, and so on. The elements which belong to such a range constitute a certain stage in our table of the ratios posit./negat. and also a layer in the interior of the earth. All this makes finally a certain conception of the structure of the nuclei rather probable, namely that they are composed so that one layer of positive units is heaped outside the others, each such layer corresponding to one stage in our table of the ratios posit./negat., except that the first stage perhaps corresponds to several layers. In such a structure each succeeding layer ought, of course, to be greater than that next within, and more so as the interior in a new stage swells by the absorption of more electrons, and we have seen indications that each succeeding stage comprises a greater range of atomic weights than that preceding it.

Of these layers, corresponding to the stages of our table, the surface-layer comprises the elements of low atomic weights up to Ca, and these elements are therefore prevalent at the surface. Element-reactions may perhaps occur in the lower parts of this layer, or did so when the surface of the earth was hot; but the pressure is not sufficient to cause the absorption of electrons in the nuclei. Those isotopes where we have to assume that electrons occur in the nuclei may come from the innermost parts of this layer, or else, as for instance in the main isotopes of argon, we may assume that atomic weights, ordinarily belonging to this layer, can still exist to some insignificant concentration in the next layer. The latter, the first deep layer, consists of metals, among which iron probably is prevalent. The composition of the other deep layers is, in consequence of their greater range of atomic weights, not so monotonous as that of the iron layer; beside heavy metals there occur light metals and metalloids. Regarding the radioactive elements, there is sometimes, to determinations of their quantity, the remark added, that if their percentage is as great in the whole mass of the earth as at the surface, the development of heat at their decomposition would more than outweigh the radiation of heat of the earth, which then would become ever hotter. According to our assumption, there would exist in the innermost part of the earth great quantities of elements which would be radioactive if they were transported to the surface, but at their original home in the interior they are components of equilibria, and thus stable, not radioactive. If elements migrate from the interior upwards, which would give rise to exothermic reactions, this is certainly counterbalanced by migrations in the converse direction and of a converse effect.

Whilst the elements of the first stage are originally at home at the surface, all others come there by migration, and those from the deepest layers must pass, intermediately, layers in which they are not stable. We must then assume that the speed of the reactions, by which they are decomposed, is small in comparison with that of their wandering. In the iron layer, for instance, there is a continual immigration of elements from below, which then are continually decomposed, and the percentage of elements from deeper layers thus established is so great that considerable masses of them have passed to the surface. Probably many quantitatively unimportant isotopes are intermediate products of decomposition, not coming from the proper layer of the element, but decomposed further so slowly that a little has been able to pass on to the surface. If the speed of wandering somewhere were much less for a certain element than it is as a rule, then this element would arrive at the surface only in a small quantity, far from corresponding to its frequency in its own layer. The wanderings of the elements may be occasioned, at least partly, by diffusion movements; therefore the speed of wandering would decrease if the element became a component of a chemical compound of a high molecular weight, and some cases where elements of similar chemical properties are rare might be explained in that way. We find two homologous elements, the manganese homologues 43 and 75, extremely rare. Each of them is followed by three elements, 44–46 and 76–78, the six platinum metals, chemically closely allied and all rather rare. No. 61 is not known and the row 62–71 consists of rare elements, all very similar to each other.

Another instance of remarkable rareness in elements we have already observed, the first element of each of the stages that we have discerned is rare, and there are indeed, at the commencement of each stage, some atomic weights missing or rare, which caused gaps in the range of the atomic weights. This is probably due to the great thermodynamic discontinuity that we assumed to divide each stage from the preceding one. The second stage commences with Sc, which is very rare for an element of so low an atomic weight; stage 3 commences with the excessively rare Ga and Ge; stage 4 probably with the very rare In; at the commencement of stage 5 there are several elements between which to choose, the most probable being Hf. That several of these introductory elements are trivalent seems only possible to be taken as a mere chance.

Still another circumstance may be mentioned here. The layers which we have assumed to be in the interior of the earth are certainly so thick that the pressure is considerably greater at their lower than at their upper border. Then in some elements different isotopes may be created in different parts in the layer, though they become well mixed afterwards through diffusion. In the second stage the percentage of electrons in the nuclei was exceptionally low in some cases, namely in Sc (corrected value) and in the chief isotope of Ni. These atoms originate probably in the uppermost part of the iron layer. Regarding Sc, which commences a stage and must be disfavoured in the equilibrium, it may be that it can only be created in this part of the layer. Regarding Ni, it may be the mixing of the isotopes that has been imperfect, in consequence of an unusually small speed of wandering.

Other cases of rareness are probably due to instability; and as this is thought to depend on the nucleus, it might seem *a priori* that no connexion with the position in the system, which is determined by the envelope, could exist. Such seems, however, to be the case at least in one instance. All isotopes of the helium gas 86 Em are excessively short-lived, and the rareness of its lower homologues may be put in connexion with this.

Here we may think of the remarkable rule, mentioned above, that isotopes of an odd atomic weight, thus positive units of weight 3, are mainly connected with elements of odd numbers. The import of the odd numbers cannot be found in the nucleus, and must therefore be sought for in the envelope. True, in the first stage the nuclei of elements of odd numbers contain as a rule an odd number of positive units; but this is not the rule in the higher parts of the system. But in the envelope every element of an odd number has an odd number of electrons. In order to comprehend that this can have an influence on the components of the nucleus, it seems altogether necessary to assume that the electrons in the envelope join in couples, or at least that their movements are connected by pairs, so that in all odd elements, but not in the even ones, an uncoupled electron would occur: without this hypothesis any real effect of the contrast odd–even cannot be imagined. That a satisfactory theory of the atom must assume a tendency of the electrons in the envelope to combine by pairs I have emphasized some years ago*. It was there the question of the outermost layer of the envelope, the valency electrons. When a metalloid gives several compounds with negative elements, as for instance chlorine, the valency stages of the divers compounds differ by two, and it was then assumed that here all electrons are joined in pairs, also, by polymerization, the odd one in elements of odd numbers; in metals the valency electrons are free. The contrast odd–even just remarked makes it necessary to assume that under the conditions of pressure and heat prevailing in the interior of the earth this tendency to join in couples is universal; the layer of the valency electrons has not any other character than the other parts of the envelope, and the difference between metals and metalloids is effaced. On the other hand, any coupling of electrons belonging to different atoms, by polymerization, perhaps an effect of the heat, does not occur. Then simply in all elements of even numbers all electrons would be coupled, and in odd ones one electron is free ; the appendage of free electrons in the envelope would be one positive unit of weight 3 in the nucleus ; of course we must then accept the hypothesis spoken of above—that the positive units are compound structures and therefore possibly to be transformed.

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* *Zeitschrift für anorgan. und allgem. Chemie,* cxi. p. 237 (1920).

In this connexion it is very noteworthy that the lowest elements up to No. 7 follow quite other rules than the others. Isotopes of odd atomic weights play an important part in 3 Li, 4 Be, 5 B, *i. e.*, in the lowest, most positive elements of the first period, but do not occur in 6 C and 7 N. It is here no question of odd or even numbers, but of positive or negative elements ; if we assume the units 3 as indicating some free electrons in the envelope, we should have in these lowest elements the very state that I assumed to prevail under normal conditions. It may then be assumed that these elements up to No. 7 belong to a lowest stage, in which the element equilibrium exists only under a small pressure—the following elements of our first stage, 8–20, created under a pressure sufficient to alter the conditions in the outermost layer of the electron envelope, but not sufficient to effect the absorption of electrons into the nuclei. It is obvious that such an outermost layer of the earth would soon cool so that element-reactions could not take place there ; then the elements belonging here could no longer be created, but they could be destroyed if they migrated to deeper layers. We find, indeed, these lowest elements up to No. 7 unmistakably rarer than most other elements of our stage 1. Our stage 1 would thus be divided into several stages, the lowest of which reaches to No. 7 ; if thus No. 8, O commences a new stage, the rule that the lowest element of a stage is rare would not be valid in this low part of the element system.

It is thought by some that elements of an odd number, as a rule, are rarer than even ones. Regarding the higher parts of the system, this would from our standpoint be explained by a greater speed of decomposition in the odd elements at their wanderings in the interior. Yet such a rule does not seem altogether manifest ; at least it is rather obscured by the many other causes of rareness in elements. But in Aston's table of isotopes it seems to be manifest that in the higher part of the system there exist, as a rule, only few isotopes of odd elements, but often very many isotopes of even ones. We have said above that many unimportant isotopes may be intermediary products of decomposition, which then would be further decomposed with a greater speed if they have an odd than if they have an even number.

The reflexions made above have, of course, significance not only with respect to the earth, but to all celestial bodies, and we shall in this connexion examine the data about the specific gravity of the planets. We find the planets, in this respect, belonging to two categories, which are to be examined separately—the small bodies with high density and the big ones with considerably less density obviously depending on the latter still being so hot that they are not bounded by solid crusts, but by envelopes of hot gases.

Regarding the former, the following table shows the values now assumed, the values for the earth being taken as unit :—

	Moon.	Mercury.	Mars.	Venus.	Earth.
Mass	0·012	0·03	0·10	0·79	1
Density	0·62	0·64	0·71	0·79	1

The specific gravity of the earth is so great, 5·6, that it has not been attempted to explain it by the compression, in the interior, of the materials of the crust, but it has been assumed that in the interior of the earth there exists a heavy nucleus of metal, which also is in accordance with the seismologic experiences. Our assumptions above are in agreement with this view, but with the addition that the formation of the nucleus of heavy elements is an effect of the pressure in the interior of the earth. The pressure depends on the mass, and therefore it is to be expected that the greater the mass of a body is, the greater will its density be. In the table above we find, indeed, such a rule conspicuously appearing, and we must regard this table as a good confirmation of our views. The increase of specific gravity with mass would firstly show that the greater the mass the greater the percentage that occupies the heavy nucleus. To explain this unequal distribution of the heavy elements in the several celestial bodies by cosmogonical causes might perhaps be possible in the case of the moon, but in the other bodies it would appear as a mere incomprehensible chance ; by our hypothesis that it is the pressure, and thus the very mass, that creates the heavy elements, the thing becomes plainly intelligible.

The density of the moon (and of Mercury) is not much greater than would be expected of compressed silicates ; still, a small metallic nucleus may be assumed. In Mars it is greater, and still more so in Venus. The difference between Mars and Venus is less than would be expected ; probably belonging to different atoms, by polymerization, perhaps an effect of the heat, does not occur. Then simply in all elements of even numbers all electrons would be coupled, and in odd ones one electron is free; the appendage of free electrons in the envelope would be one positive unit of weight 3 in the nucleus; of course we must then accept the hypothesis spoken of above—that the positive units are compound structures and therefore possibly to be transformed.

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The density of the moon (and of Mercury) is not much greater than would be expected of compressed silicates; still, a small metallic nucleus may be assumed. In Mars it is greater, and still more so in Venus. The difference between Mars and Venus is less than would be expected; probably the interior of Mars is cooled down rather much, and is far less hot than the interior of Venus. The seismologists seem to estimate the thickness of the silicate mantle of the earth as about 1500 kilometres; the heavy nucleus would then occupy about 40 per cent. of the total volume. In Venus the outermost layer is, of course, thicker, the percentage of the nucleus less than in the earth; but we have certainly to assume, too, that in the earth the heavy interior layers of the nucleus occupy a percentage of the volume that gives them a considerable influence on the specific gravity of the planet, whilst in Venus their influence is little.

Regarding the big planets, including the sun, which are surrounded by an envelope of hot gases, the matter is more complicated. On the one hand, the pressure, depending on the mass, raises the specific gravity; on the other hand, the temperature of the gaseous surface lowers it. The temperature depends on the degree of cooling at which the body has arrived, and the greater the mass, the less is the speed of the cooling. The mass acts thus in two ways directly opposed to each other. In the cases of the sun and of Jupiter, the effect of the greater pressure and the higher temperature of the sun outweigh each other; the specific weight of the two bodies is well-nigh identical. Uranus, the mass of which is about 5 per cent. of that of Jupiter, has a somewhat lower density than the latter; whilst Neptune, the mass of which is nearly equal to that of Uranus, has a rather high density, probably depending on Neptune, the remotest of the planets, having had a longer time than the others to cool.

Saturn, with about one-third of the mass of Jupiter, has a specific gravity little more than the half of that of Jupiter. This value does not seem to fit into the table, and it is probably to be assumed that some peculiar circumstance has influenced this planet. We may think of the so-called *nova* phenomena. A star blazes up very suddenly, but the brilliancy of it disappears again very soon; it is thus a phenomenon of rather small importance in the history of the star. The most usual explanation seems to be that a body, surrounded by a gaseous envelope that is already somewhat cooled and therefore shining only feebly, by an eruption from within gets the gaseous envelope torn asunder for a moment, so that hot layers in the interior become visible until the envelope has collected again. The old state, however, cannot be totally restored at once; the eruption has transported an appreciable quantity of heat up to the exterior gaseous envelope, which therefore for a considerable time is hotter and thus thinner than that corresponding to the real equilibrium, and an abatement of the apparent density of the measure that we observe in Saturn might very well be the consequence. It may be emphasized that this very planet has another unique peculiarity too, namely the ring, which, of course, makes it still more probable that Saturn alone among the planets shows the marks of some peculiar agency.

We may finally mention the meteors. These are thought to have come from a planet which eventually became shattered. The meteoric stones would then come from its silicate mantle, the irons from its nucleus. As very heavy metals do not seem to occur there, this nucleus may only have been equivalent to the outermost part of the nucleus of the earth, and the astronomers seem indeed to assume this planet to have been rather small. To explain in detail the composition of the meteoric irons, iron and a little nickel, is difficult, as there seem to exist several possibilities, between which we cannot decide. To mention only one possibility, the asteroid planet may have already cooled so that element-shaping reactions did not occur in the nucleus or the magma basins which the irons came from, and the constituents had then emigrated intc the silicates so that beside the main component, iron, there remained only nickel, which, as we have already mentioned, was perhaps hampered in its movements.

Addendum.—In the above paper, in the last section dealing with the astronomical data for the masses and specific weights of the planets, the values (taken from the Almanac for 1928 of the Swedish Academy of Science) vary much in their reliability ; this I did not take sufficiently into account, and therefore the following may be added :—

Of the planets bounded by solid crusts the values for the earth, Mars, and the moon, which fit our assumptions well, are certainly exact. For the planets which have no satellites the values are not so trustworthy. The values for Venus still do not vary greatly : it seems certain that both mass and density are somewhat lower than those of the earth, but the value 0·79 for the density is perhaps too low ; a somewhat higher value would in reality fit our system better. For Mercury values varying from 0·64 to 3 are to be found ; it seems necessary to omit this planet, the data being too variable.

As regards the bodies bounded by envelopes of hot gases, the most probable values for the densities of the Sun, Jupiter, Uranus, and Neptune seem to be about 0·25 ; the values for Uranus and still more for Neptune are yet somewhat varying ; the very different value for Saturn 0·13, as commonly given, is certainly reliable.

LXXXIII. *The Spectrum emitted by a Carbon Plate under Bombardment.* *By* A. A. NEWBOLD, *B.Sc.* *

MOST of the experiments on the radiation which fills the gap between the two groups which are amenable respectively to X-ray crystal and ordinary grating methods have dealt with the conditions of excitation of such radiation. As a rule the radiation emitted from various elements under the bombardment of electrons from a glowing filament has been measured by its photoelectric effect on a target of some metal, such as copper, nickel, etc. The accelerating or bombarding potential is usually varied in steps, and the total radiation measured at each step by means of its total photoelectric effect, the latter being determined by some such means as the charging-up of an electrometer connected to the insulated target. These photoelectric currents divided by the corresponding thermionic currents are then plotted against the accelerating voltage producing them. If, now, there is present characteristic radiation superposed upon the general radiation, it is to be expected that at the characteristic voltage which just excites this radiation there will be some kind of a discontinuity, such as a kink or change in slope of the curve.

Whilst the method thus outlined is valuable, it has considerable limitations, and its results require simplification and also restriction by comparing with those given by other methods. In particular, it almost certainly yields discontinuities at potentials which are not excitation potentials, properly speaking, at all †, and it gives no information whatever as to the frequencies or distribution of energy in frequency of the radiation excited. In fact, it tells little or nothing about the character of the spectrum produced.

The method of the present experiments is different. The primary exciting voltage is now kept constant, and, in fact, all the conditions of operation of the part of the tube generating the radiation are kept as constant as possible. The radiation generated is allowed to pass through an appropriate ion filter into an adjacent chamber, where it falls on a small electrode at the centre of a large spherical electrode. An electric field is maintained between the electrodes, and is so directed as to oppose the motion of the photoelectrons ejected from the central electrode. The potential difference V between the electrodes is increased or diminished in steps, and the current of electrons is measured which is able to pass through this field to the surrounding electrode. The central electrode being small and the field radial, the condition that an electron ejected with velocity v shall contribute to the current is

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* Communicated by the Author.

† For a fuller discussion see O. W. Richardson and F. C. Chalkin, Roy. Soc. Proc. A, cx. p. 247 (1926).

$$\tfrac{1}{2}mv^2 \geqq eV. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The experiment thus determines, at least very approximately, the distribution of kinetic energy among the emitted electrons. But it is well known that when monochromatic radiation of frequency ν falls on a metal, electrons are emitted with all velocities not exceeding the abrupt limit set by the equation

$$\tfrac{1}{2}mv^2 = h(\nu - \nu_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where ν_0 is the threshold frequency of the metal. If our experiment were performed with such a monochromatic radiation, the result would be zero current for all values of $V > \frac{h}{e}(\nu - \nu_0)$, and for $\frac{h}{e}(\nu_1 - \nu_0) > V > 0$ the current plotted against V is the function which represents the integration of the energy distribution function with respect to energy. In general, we have to deal with a mixture of a general radiation and a number of monochromatic radiations of frequency ν_1, ν_2, etc.; so that we expect the experimental curve to arise from the superposition of a number of such curves on the continuous curve due to the general radiation. This curve should have a discontinuous change of slope at each of the successive values of V equal to $\frac{h}{e}(\nu_1 - \nu_0)$, $\frac{h}{e}(\nu_2 - \nu_0)$, etc., and thus enable us to pick out the monochromatic constituents ν_1, ν_2, etc. present in the radiation. The method might be misleading if the rise of photoelectric current with voltage after passing the critical voltage for monochromatic radiations were very gradual, in which case the discontinuities would be systematically displaced, or if the energy-distribution function for electrons liberated by monochromatic radiation were too complicated, in which case there might be too many discontinuities. However, our present knowledge of such phenomena does not lead us to anticipate the existence of these difficulties, except perhaps as occasional accidents.

This method was first used in this region of the spectrum by Richardson and Bazzoni *, who tried it in dealing with

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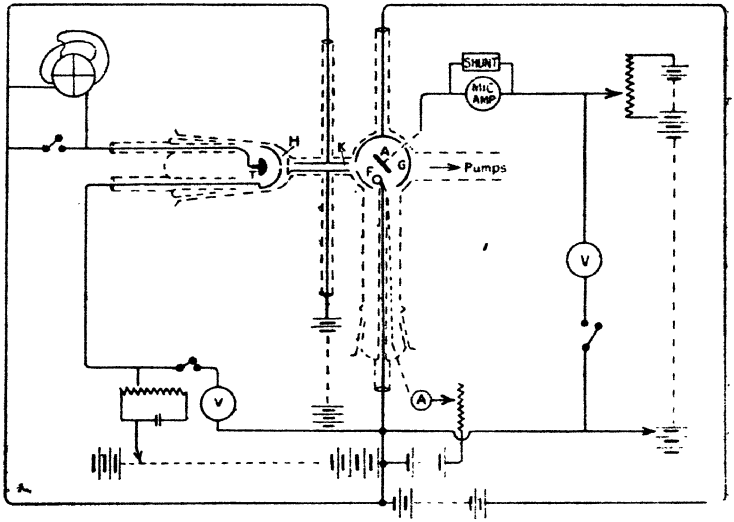
* Phil. Mag. xxxii. p. 426 (1916); xxxiv. p. 285 (1917).

the radiations from various gases and vapours. It was not very satisfactory in that application, on account of difficulties introduced by the gases necessarily present. It has since been improved and applied to the detection of soft X-rays by Lukirsky[*]. The results of the present investigation suggest that it is capable of development into a method of considerable precision.

A plan of the tube is shown drawn to scale in fig 1 *a*. It is made of transparent quartz glass, so that it and the enclosed electrodes can be thoroughly and conveniently baked out. The connecting wires are brought out and soldered to metal caps which are cemented to the quartz with sealing-wax. The quartz tube is also connected to the glass connexion of the evacuating apparatus by a sealing-wax joint.[*] The filament F is heated by a set of accumulators with a rheostat and ammeter in series. The accelerating potential from the filament F to the anode A is provided by a large battery of 300 accumulators in series. In order to keep this potential constant, the last section of the accumulators is shunted by a coil of bare wire wound on an open frame, and the potential taken from a contact which can move continuously along

Fig. 1.



Apparatus.

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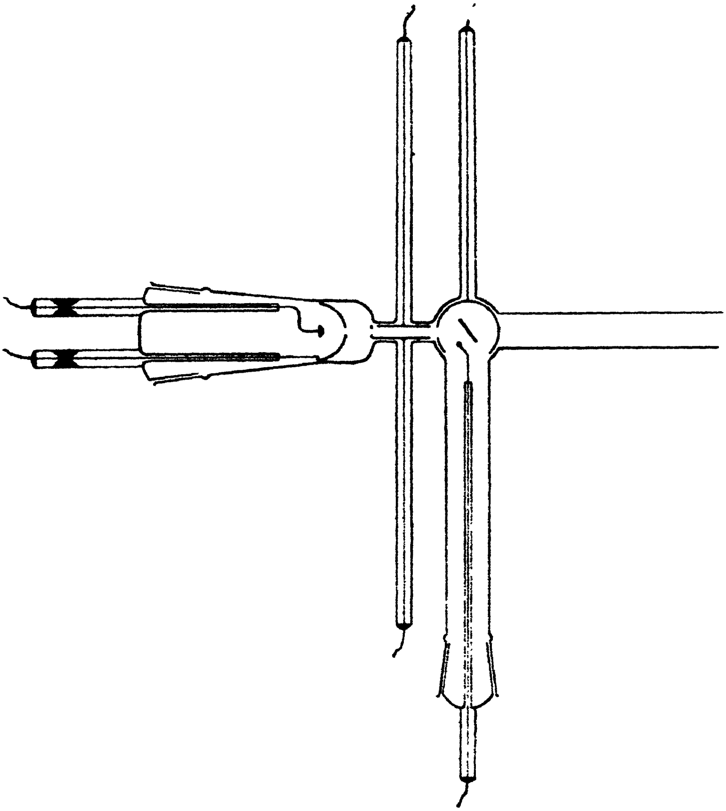
[*] Phil. Mag. xlvii. p. 466 (1924); *Zeits. f. Physik*, xxii. p. 351 (1924).

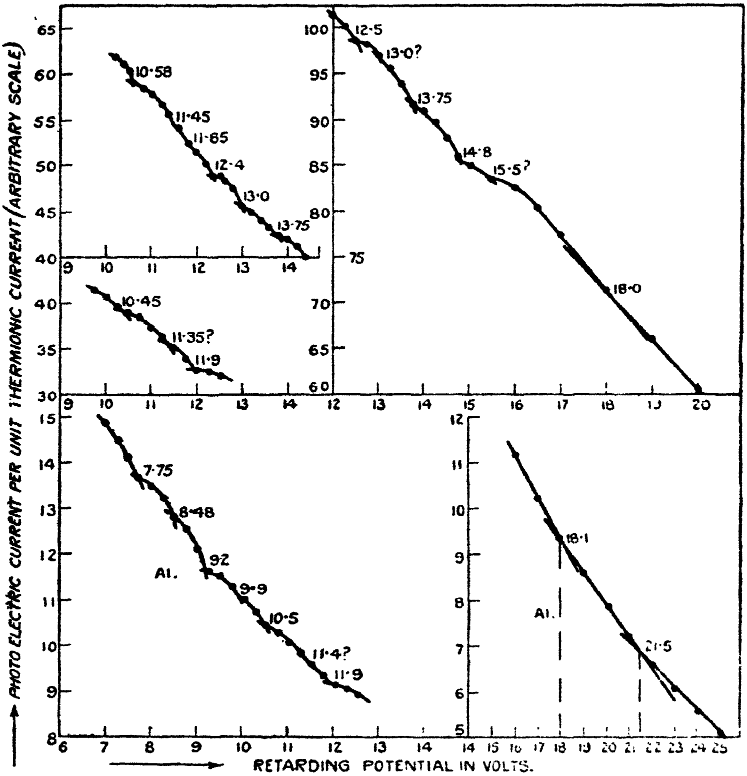
the wire and is set so as to maintain a constant reading on the voltmeter connected across the gap FA. This circuit also includes a suitable micro-ammeter for measuring and controlling the thermionic current. The guard electrode is of copper and is cylindrical in shape, with the requisite holes for the escape of the radiation and the admission of the leads and supports for the electrodes A and F. Its function is to stabilize the accelerating field, and it is kept at a potential slightly negative with respect to F, so as to drive back any electrons tending to pass into the measuring chamber. The radiation passes through between the condenser plates K. These plates are kept at a potential difference of 200 volts to filter out any ions present in the stream of radiation. The potential difference which it is necessary to apply is ascertained by taking a saturation curve for the current across

Fig. 1 *a*.



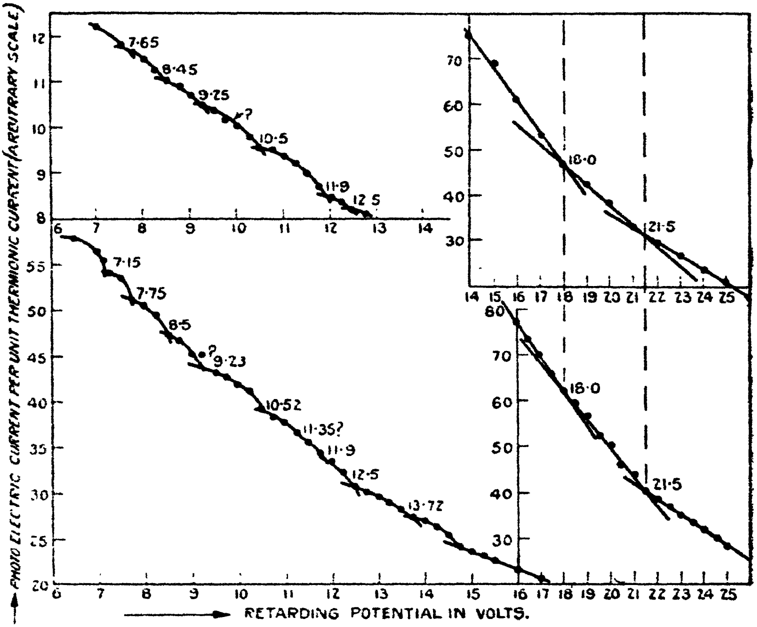
the gap between the plates K under the working conditions. The radiation passes through the small rectangular slit in the hemisphere H and strikes the photoelectric target T which is connected to one pair of quadrants of an electrometer. Both the electrode H and the target T are of copper. The retarding potential is applied between H, and the other pair of quadrants of the electrometer from dry cells, a fine adjustment being provided by means of a potentiometer across a 2-volt accumulator. All the electrostatic measuring apparatus and connexions are shielded in the usual way. The apparatus is exhausted during operation by means of an ordinary backing pump, a rotary oil pump, a mercury vapour pump, and two liquid air traps, the last one being filled with charcoal. These evacuating devices are all in series.

Fig. 2.



The element chosen for the present investigation was carbon, the target T being cut from an arc lamp carbon and having the dimensions 16 × 10 × 1·5 mm. The apparatus was first of all highly exhausted, and the vacuum kept up by running the pumps during the readings. The quartz tube was then baked out properly to drive out occluded gas, and the anode for the same purpose brought to a red-heat several times by bombarding from the filament with about 3000–4000 volts obtained from a transformer. After this the filament current was switched on and a constant accelerating potential, which was usually 300 or 600 volts, was applied. The filament current was adjusted, and through it the

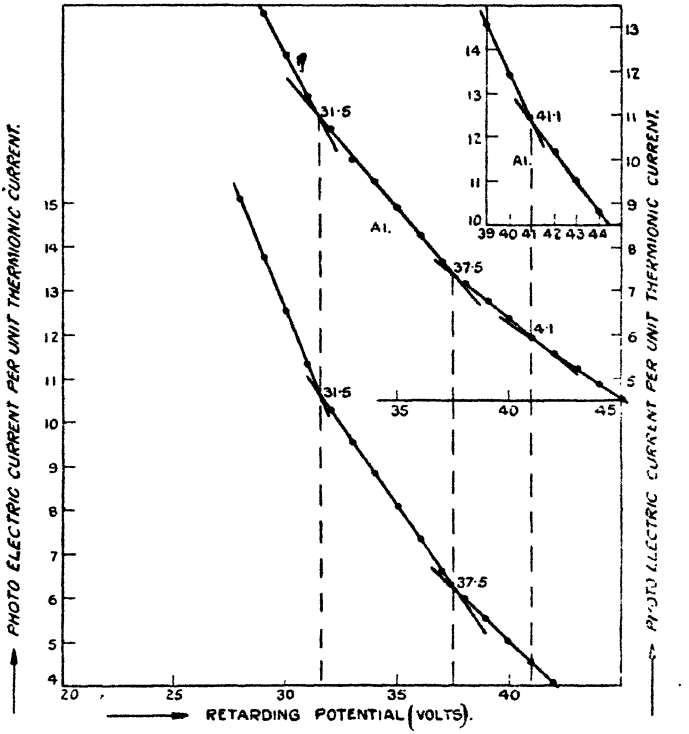
Fig. 2 *a*.



thermionic current, so that the rate of deflexion of the electrometer was most suitable for accurate measurement. The whole apparatus was then left until any more gas which might have been driven off from the filament and other parts of the apparatus near it had been removed and the high vacuum was steady, and until the thermionic current had been steady for some time. As a rule, the tube was run for one or two hours before taking observations, and no readings were taken unless a vacuum of between 10^{-7} and 10^{-8} cm. was attained and electrical conditions steady; under these conditions readings were entirely reproducible. The photo-electric current for varying retarding potentials was then observed and a curve plotted between these variables. At first the voltage was varied in steps of one or two cells, these being reduced latter to 1 volt, $\frac{1}{2}$ volt, and $\frac{1}{4}$ volt, and ultimately to $\frac{1}{10}$ volt. The current was measured by timing the deflexion of the electrometer whose sensitivity was 1400 divisions per volt.

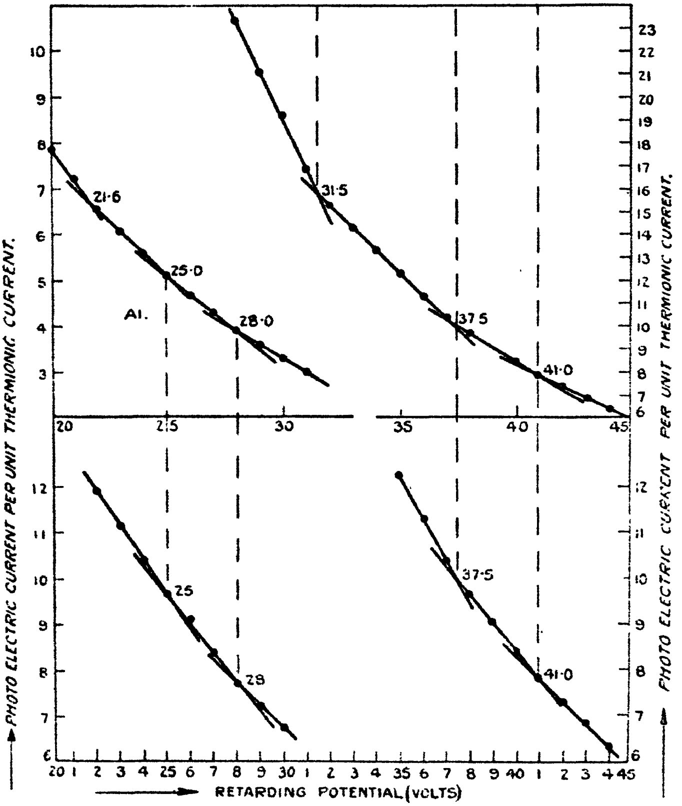
With the apparatus as described the deflexion of the electrometer is, in general, in the opposite direction from that

Fig. 3.



to be anticipated from the considerations which have hitherto been brought forward. This appears to be due to electrons emitted by the photoelectric action of the radiation on the edges of the slit in H and the adjacent ends of the condenser plates K. The current is composed of the true photoelectric current and electrons from the outer electrode which are driven by the field on to the target. This latter opposes the true current, and with any but low retarding potentials swamps it so as to give an apparent "positive" effect. At any rate, this trouble has been removed by putting one of the plates K at zero potential and the other at a positive potential. The end of the positively-charged plate is then bent round at right angles and a slit cut in it rather smaller than the slit in H. The effect of these measures is to prevent the radiation from reaching the edges of the slit H and to introduce a retarding field for electrons between H and K.

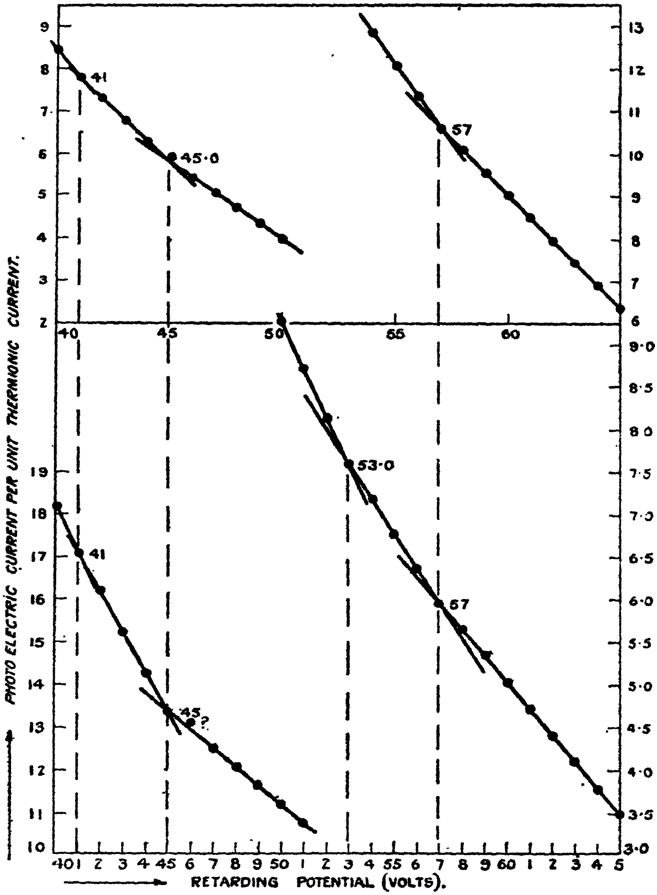
Fig. 3 *a*.



Under these conditions the effects observed are remarkably sharp and entirely reproducible, and the observed discontinuities seldom appear to vary in position by $\frac{1}{10}$ volt.

Some of the results are exhibited in figs. 2–4. Figs. 2 and 2 *a* contain the phenomena from 6 to 25 volts, figs. 3 and 3 *a* those from 20 to 45 volts, and figs. 4 and 4 *a* those from 46 to 65 volts. In all these plots every single experimental point is marked; there are no omissions or other corrections or adjustments. Below about 15 volts it will be observed that the graphs consist of intersecting portions of curves which are individually concave to the voltage axis; above 15 volts this feature disappears, the curves becoming intersecting straight lines.

Fig. 4.



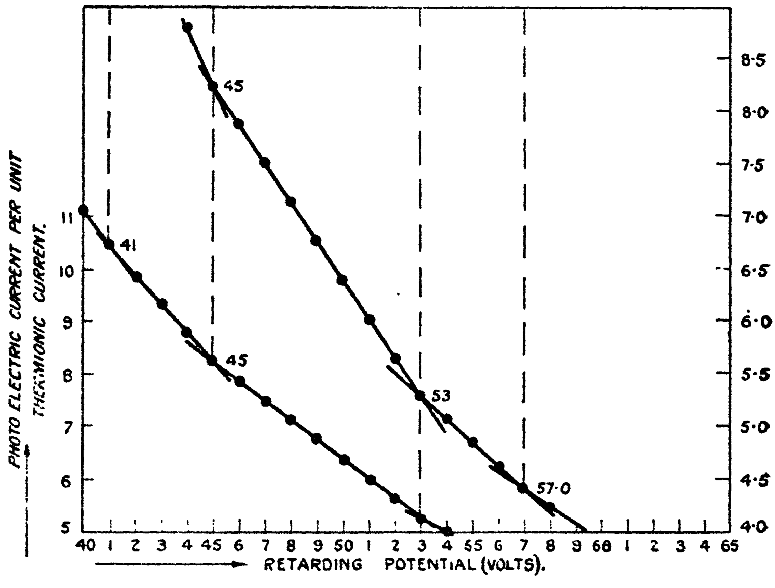
Let K be the contact potential difference between T and H, and let ν_0 be the threshold frequency of the material of T; then if there is, in the radiation falling on T, a monochromatic constituent whose frequency is ν_s, we shall, according to the foregoing discussion, expect a discontinuity in graphs such as those of figs. 2–4 *a* at the potential V_s, as read on the voltmeter, which satisfies

$$\epsilon(V_s+K)=\tfrac{1}{2}mv^2=h(\nu_s-\nu_0), \quad . \quad . \quad . \quad . \quad (3)$$

V_s+K being the actual potential difference which reduces the maximum velocity of electrons liberated by this radiation to zero; so that the frequencies of the monochromatic radiations should be given for every V_s by

$$\nu_s=\nu_0+\frac{e}{h}(V_s+K). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Fig. 4 *a*.



The value of ν_0 for copper has been measured by Richardson and Compton * as 10^{15} sec.$^{-1}$, or the equivalent of 4·12 volts. As the surfaces both of T and H were of copper in the experiments, we should anticipate that K would be zero, so that the observed V_s would require correction by the addition of the quantity of $\frac{h}{e}\nu_0$ or 4·12 volts.

Before adding this correction, however, these measures were compared with the frequencies of the lines of the carbon spectrum in the part of this region where they have been found and measured by Millikan and Bowen on the vacuum grating spectroscope. It is to be remembered that Millikan and Bowen's spectrum was generated by hot sparks between arc carbon electrodes, and is therefore presumably that of an electrically-excited gas of more or less familiar type. There does not appear to be any *a priori* method of knowing how close a correspondence to anticipate between such a spectrum and that generated by the impact of electrons on the same substance in the solid state. It was rather surprising to find that the spectrum was coincident with that of Millikan and Bowen, provided no correction whatever was made for the work done by the electrons in getting out of the copper. This can be seen from Table I., in which the first column gives the critical voltages as measured without any correction, and the second and third columns are the corresponding wave-lengths and wave-numbers as given by the quantum relation. The fourth column contains the lines or groups of lines (where the resolution is insufficient) from Milllikan and Bowen's table, which are close to these discontinuities. The last column gives the difference between their numbers and the corresponding measures obtained in these experiments. Of the 76 lines between $\nu=54{,}561$ and $\nu=277{,}408$ attributed to carbon by Millikan and Bowen, only 25 are contained in Table I., but they include every line of intensity greater than 6 and most lines of any outstanding strength compared with neighbouring lines anywhere in that spectrum. Except for the three lines of highest frequency corresponding to discontinuities at 25·0, 28·0, and 31·5 volts, there is no discrepancy amounting to as much as 0·2 volt. Even at the three highest frequencies corresponding to 25·0, 28·0, and 31·5 volts the discrepancy is not very great. The exact values for the weak inflexions at 25·0 and 28·0 volts may be difficult to ascertain, and there is something peculiar about the inflexion at 31·5, which was not resolved from 37·5 in the earlier observations, although it should have been as far as one could expect. If the above measures and Millikan and Bowen's are plotted on two scales, it does not seem possible to effect any similar set of coincidences in any other position obtained by sliding the scales past each other. Such a movement would correspond to the addition or subtraction of a linear correction such as that for the work function of copper. It appeared then, at first, as if the discontinuities occurred at voltages which, without any correction, were equivalent on the quantum relation to Millikan and Bowen's frequencies.

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* Phil. Mag. xxiv. p. 586 (1912). There is a second determination giving a value 3 per cent. lower.

On examination of some of the earlier curves it was noted that for the low retarding potentials no drop in the photo-electric current was observed until a retarding potential of 4·1 volts had boen reached, when the current immediately began to drop. Further experiments showed that there was a constant accelerating force superimposed on the retarding field of the sphere by the positive potential on the condenser plate and shield. This, by a strange coincidence, was almost exactly equal to the threshold value V_0 of 4·12 volts. (This held whether the target was made of copper or of aluminium,

TABLE I.

Volts (V_s).		λ (Å.U.).	ν (wave-number).	Millikan & Bowen. ν	(Int.).	Diff.
(ν_0 for Cu.)	*4·12*	*3,000*	*3,333*			
weak.	7·05	1752	5,705	5,706·8	(2)	— 1·8
	7·66	1613	6,200	6,032·8	(5)	+ 167·8
				6,404·8	(5)	— 204·8
	8·47	1459	6,850	6,832·0	(2)	+ 18·0
	9·23	1338	7,480	7,490·9	(15)	— 10·9
				7,554·4	(7)	— 74·4
weak.	9·88	1250	8,000	8,015·8	(7)	— 15·8
	10·51	1174	8,510	8,506·2	(15)	+ 3·8
weak.	11·4	1083	9,230	9,152·2	(3)	+ 77·8
				9,381·2	(8)	— 151·2
	11·88	1030	9,710	9,646·1	(11)	+ 63·9
				9,899·0	(10)	— 189·0
	12·47	992	10,080	10,234·3	(12)	— 154·3
weak.	13·0		10,515	10,575·2	(4)	+ 60·2
	13·71	901	11,100	11,060·6	(10)	+ 39·4
	14·74	838	11,920	11,648·1	(5)	+ 271·9
				11,787·6	(0)	+ 132·4
				12,346·4	(5)	— 426·4
				12,395·7	(6)	— 475·7
				12,501·6	(5)	— 581·6
	18·0	687	14,540	14,549·1	(8)	— 9·1
	21·5	575	17,400	17,405·2	(6)	— 5·2
weak.	25·0		20,250	20,014·0	(4)	+ 236·0
weak.	28·0		22,660	21,755·2	(6)	+ 904·8
strong.	31·5		25,500	25,882·6	(4)	— 382·6
strong.	37·5		30,380			
	41·0		33,200			
strong.	45·0		36,450			
strong.	53·0		42,900			
	57·0		46.200			

as is mentioned later.) There was present, in fact, a state of affairs akin to the plate and grid of a thermionic valve. This effect then just balanced the threshold function and made any correction of the recorded values unnecessary.

In the foregoing it has been assumed, to simplify the discussion, that the electrons emitted from the electrode T were ejected, by the radiation from the carbon target, from the superficial levels which supply the electrons in the photoelectric effect as ordinarily observed in the ultra-violet. They might, however, arise from the action of X-rays of higher frequency, let us say ν_c, from the carbon target on electrons in the M-level of copper, in which case the observed discontinuities would be at voltages equivalent to $h(\nu_c - \nu_{m_1})$, $(\nu_c - \nu_{m2})$, etc., where ν_{m1}, ν_{m2}, etc. are the frequencies corresponding to the M-thresholds for copper. In such a case the voltages of the observed discontinuities would depend on the material of T as well as of the target A. This matter has been put to the test by repeating all the observations with an aluminium electrode at T instead of the copper electrode. Some of the curves so obtained are shown in figs. 2–4 *a*, marked Al. It will be seen that the discontinuities occur at exactly the same place with the aluminium as the copper electrode. At first sight it might be thought that even if the electrons were generated from the most superficial levels, the apparent discontinuities would be shifted owing to the introduction of the contact-electromotive force between aluminium and copper. This is not the case, however, for the effect of the contact potential difference in reducing the energy of the emitted electrons is just counterbalanced by the extra energy got owing to the reduced work function, with the result that the stopping potential with illumination of assigned frequency is independent of the nature of the metal illuminated*. All the discontinuities given in Table I. are present both with the copper and with the aluminium electrodes, except that the three weak inflexions at 7·05, 9·88, and 11·4 volts have not been recognized on the aluminium graphs. This does not necessarily prove that they are specific to copper, as they are not detectable on all the copper graphs. The rest must without doubt be carbon lines. Most of the measurements have been made with 600 volts on the X-ray generating tube, but many sets have been taken at 480, 300, and 240 volts, and one determination of the discontinuities below 20 volts has been made with 120 volts only between F and A in fig. 1.

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* Richardson & Compton, Phil. Mag. xxiv. p. 575 (1912).

Summary.

This paper describes an electrostatic method of investigating soft X-ray spectra and its application to the spectrum emitted by a carbon plate under electron bombardment up to 600 volts. Over the frequency range 5700 to 26,000 the spectrum found is either identical with or at least resembles very closely that mapped by Millikan and Bowen for gaseous carbon.

In conclusion the writer wishes to express his thanks to Dr. H. T. Flint, who assisted in the early stages of the work.

LXXXIV. *The Magnitude of Non-Dimensional Constants.*

By W. N. Bond, *M.A.*, *D.Sc.*, *F.Inst.P.*, *Lecturer in Physics in the University of Reading* [*].

THE problem here discussed may have been considered before by other writers, but absence of any treatment of, or definite reference to work on, the subject in current Physics literature is thought to be sufficient to justify the present paper [†].

The "constants" occurring in physical equations may be classified thus :—(1) Universal constants, such as the velocity of light in a vacuum ; (2) specific constants, such as the thermal conductivity of copper ; (3) arbitrary constants, such as the number of degrees in a right angle; and (4) numerical constants, such as $3/2$, π, $\sqrt{2}$. This last type of constant is the one here considered.

These numerical constants occur as multiplying factors in equations such as that for the volume of a sphere

$$V=\frac{4}{3}\pi r^3,$$

and are very often ratios geometrical in their origin. They may sometimes be less easily deduced theoretically, as in the case of the capacity of a pair of conducting spheres placed in contact but at a distance from other bodies. The form of the equation may frequently be predicted from dimensional considerations ; and it might be convenient if the order of magnitude of the constant involved could also be predicted before it was obtained by detailed theory or experiment.

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[*] Communicated by the Author.

[†] Reference may be made to Einstein, *Ann. der Physik*, xxxv. p. 687 *et seq.* (1911).

It is known from experience that these numerical constant multiplying factors do not often differ very greatly from unity in value. Also it is known that, for any one greater than unity, there is automatically the reciprocal value less than unity. If, with the values of the numerical constants as abscissæ, a frequency distribution curve be drawn, it will be skew and limited in one direction (at zero). If the logarithms of the constants had been used as abscissæ, a symmetrical curve extending to infinity in both directions would have been obtained.

For the construction of the curve, the numerical constant multiplying factors (including unity) were collected by random selection from physical equations from eleven different sources, giving 731 values above unity (and their reciprocals below unity). It was found that the fraction falling between 2 and 1/2 in value was 733/1462 (*i. e.*, differing from 1/2 by less than the error of sampling). Using Peters's formulæ, it was attempted to fit a normal law of errors curve to the symmetrical distribution obtained by taking the logarithms of the constants as abscissæ. The curve thus obtained corresponded to half of the constants falling between 2·18 and 0·459 in value. It was found, however, that the observations were definitely in better agreement with the following hypothesis:—that the constants less than unity were distributed in value uniformly between 0 and 1 (with the corresponding distribution from 1 to ∞). This theory is compared with the experimental results in the following table:—

Range of values of the constants.	Calculated.		Observed.
	Fraction in the range.	Number in the range.	Number in the range.
0 to 1/3	1/6	243·7	245
1/3 to 2/3	1/6	243·7	237
2/3 to 1	1/6	243·7	249
1 to 2	1/4	365·5	366·5
2 to 4	1/8	182·8	187·5
4 to 8	1/16	91·4	95
8 to 16	1/32	45·7	42·5
16 to 32	1/64	22·8	25
32 to 64	1/128	11·4	11·5
64 to ∞	1/128	11·4	3

Apart from the fact that the proposed theory predicts rather more values over 64 (and similarly under 1/64th) than were observed, the observations and theory are in very close agreement. This agreement and the very simple nature of the suggested law make it seem likely that, in general, this law is applicable to the non-dimensional numerical (but not arbitrary) constants which occur as multiplying factors in equations arising in physical calculations. (It is not suggested that the law applies to the numerical multiplying factors which occur in the various terms of an expansion in the form of a mathematical series.) The probability, then, of any such constant chosen at random falling in value outside the range (1/3 to 3) is 1/3, and so on.

University of Reading,
Department of Physics.
7th January, 1929.

LXXXV. *A Complex Pendulum driven by Two Pendulums having Commensurate Periods.* *By* H. M. BROWNING, *M.Sc., Ph.D.*[*]

[Plates XVI. & XVII.]

IN previous papers[†] the author has analysed theoretically and verified practically the motions set up in pendulums when two or more were coupled together. Also the effect of resonance has been shown when one or more pendulums have acted upon several responders. In the latter, either the aggregate effect over a long period or the instantaneous effect has been obtained. No record of the actual motion with time of one pendulum has been shown. In connexion with a practical problem, it was thought desirable to have such a record, and so the work described below was undertaken. Thus in the present instance the aim was to obtain records of a complex pendulum when it was subjected to external vibrations of different frequencies acting at the same time. During one set of experiments the ratio of the periods of the compound-responding pendulum was kept constant, as well as the ratio of the driving pendulums, but the actual periods of the latter were altered between wide limits.

These pendulum experiments reproduce the motion of phase swing that will take place in a synchronous electrical machine subjected to a periodically fluctuating load. It is well known that an alternator working in parallel with other alternators is subject to such phase swinging, and that the period of the swing is a definite quantity which can be calculated with fair accuracy for any given machine. The same also applies to a synchronous motor and to a rotary-converter which is fed on its A.C. side. This latter machine, particularly, is subject to fluctuating loads, especially when it is used for traction work.

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[*] Communicated by the Author.

[†] Phil. Mag. (6) xxxiv. pp. 246–270 (Oct. 1917); xxxvi. pp. 169–178 (Aug. 1918); xxxvii. pp. 453–455 (April 1919); xliv. pp. 573–576 (Sept. 1922).

In practice, the load curve will consist of a number of sharp, unrelated peaks, but occasionally it happens that a series of such peaks may occur at fairly regularly-spaced intervals. In such a case the load will correspond to a sinusoidal load whose period is fixed by the time interval between the successive peaks, with a number of harmonics superposed. The mechanics of the machine is thus similar to that of a pendulum having definite free periods acted on by a series of forces with periods in the ratio $1 : \frac{1}{2} : \frac{1}{3}$, etc. The amplitudes of all but the fundamental and one of the harmonics may be in some cases negligible, and then the motion is that of a pendulum acted upon by two external forces having commensurate periods.

Experiments on the rotary-converter loaded in this manner have shown that the motion of phase swing is very similar to that of the pendulums previously described, especially if the damping of the rotary-converter is small, as it was in the experimental machine.

Theory.

The complex pendulum was made on the principle of the cord and lath pendulum described in the Phil. Mag., Oct. 1917.

At the end of a long light wire a small loaded aluminium bucket, with a hole in the bottom, was attached. At a fixed point on the wire a weight was fastened. Salt was allowed to run slowly from the bucket, and the weights and lengths adjusted so that, when vibrating freely, the pendulum oscillated with two frequencies, which were in a simple ratio, and which remained approximately constant in spite of the loss of salt (this is considered more fully later).

Using the same notation as in equations (55) and (56), p. 259, Phil. Mag. xxxiv. Oct. 1917, the two following equations are obtained for the motion of the pendulum :

$$\mathrm{P}\frac{d^2y}{dt^2} + \mathrm{P}m^2y = \mathrm{P}m^2\alpha z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Q}\frac{d^2z}{dt^2} + \{(\mathrm{P}\alpha + \mathrm{Q})n^2 + \mathrm{P}\alpha^2m^2\}z = \mathrm{P}m^2\alpha y. \quad . \quad (2)$$

As solution

$$y = e^{xt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$z = \frac{x^2 + m^2}{m^2 \alpha} e^{xt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Then

$$Qx^4 + Qm^2x^2 + \{(P\alpha + Q)n^2 + P\alpha^2m^2\}\, x^2 + \{(P\alpha + Q)n^2 + P\alpha^2m^2\}m^2 = Pm^4\alpha^2,$$

i. e.

$$x^4 + \{(M\alpha + 1)n^2 + (M\alpha^2 + 1)m^2\}x^2 + (M\alpha + 1)m^2n^2 = 0, \quad . \quad (5)$$

where $M = P/Q.$

Thus, if $\pm ip$ and $\pm iq$ are the roots of equation (5),

$$p^2 + q^2 = (M\alpha + 1)n^2 + (M\alpha^2 + 1)m^2,$$

$$pq = \sqrt{(M\alpha + 1)}\,.\,mn\;;$$

$$\therefore \quad p + q = \sqrt{\{(M\alpha + 1)n^2 + (M\alpha^2 + 1)m^2 + 2mn\sqrt{(M\alpha + 1)}\}},$$

$$p - q = \sqrt{\{(M\alpha - 1)n^2 + (M\alpha^2 + 1)m^2 - 2mn\sqrt{(M\alpha + 1)}\}}.$$

If $\alpha = 1$,

$$\frac{p}{q} = \frac{\sqrt{\{(M + 1)(n^2 + m^2) + 2mn\sqrt{(M + 1)}\}} + \sqrt{\{(M + 1)(n^2 + m^2) - 2mn\sqrt{(M + 1)}\}}}{\sqrt{\{(M + 1)(n^2 + m^2) + 2mn\sqrt{(M + 1)}\}} - \sqrt{\{(M + 1)(n^2 + m^2) - 2mn\sqrt{(M + 1)}\}}}. \quad . \quad . \quad . \quad (6)$$

Values of M, m, and n can be chosen to make the ratio p/q whatever is desired, and in the most suitable manner.

The actual position at time t of the bucket would be given by a formula of the form

$$y = E \sin (pt + \epsilon) + F \sin (qt + \phi), \quad . \quad . \quad . \quad (7)$$

the values of E, F, ϵ, and ϕ being determined by the initial conditions.

No damping factor is introduced into the above equations, as this was found to be negligible with the apparatus used.

Now, if two impressed forces of value $G \sin \omega t$ and $H \sin x\omega t$ are applied to this complex pendulum, we can consider the latter as having two free periods of frequencies

$$\frac{p}{2\pi} \text{ and } \frac{q}{2\pi}$$

The equation of motion of this pendulum is

$$\left.\begin{aligned} P\ddot{y}+Pm^2y-Pm^2z &= F\sin\omega t+G\sin x\,\omega t, \\ Q\ddot{z}+\{(P+Q)n^2+Pm^2\}z-Pm^2y &= F\sin\omega t+G\sin x\,\omega t. \end{aligned}\right\} \quad . \quad . \quad . \quad (8)$$

It would be found that the solution of these equations would be of the following form :—

$$\left.\begin{aligned} y &= A\sin(\omega t+\alpha)+B\sin(x\,\omega t+\beta) \\ &\qquad +C\sin(pt+\gamma)+D\sin(qt+\delta) \\ \text{and}\quad z &= A'\sin(\omega t+\alpha')+B'\sin(x\,\omega t+\beta') \\ &\qquad +C'\sin(pt+\gamma')+D\sin(qt+\delta'). \end{aligned}\right\} \quad (9)$$

z and y give the motion of the bob and the bucket ; thus, as the motion of the latter is the only one required, we need not consider the second equation of (9).

The values of the constants A, α, B, etc., may be obtained from equation (8). If ω or $x\omega$ is equal to p or q, resonance will occur, and the effect of this vibration will be so great that any others will be masked.

If damping had been taken into consideration, equation (9) would have required a slight alteration, as p and q would have been modified by the damping factor.

Experimental Arrangement.

The apparatus shown in fig. 13, Pl. V., "Coupled Vibrations," Phil. Mag., July 1918, was adapted for the response of a complex pendulum to two drivers. Figs. 1 and 2 give the side and end elevations of the actual arrangement used. Two stout cords ACB and DEB, as shown in fig. 1, are arranged to be parallel between E and B. At C and E pendulums M and N, with heavy bobs (approximately 2 kilograms), are hung. At S there is a light inflexible stay ; at the middle of this is slung the light complex pendulum R, as shown in fig. 2. Under R a board is drawn along, so that a record of the lower bob of R can be made by salt which runs from it.

The point C was placed over a trap-door in the Research Room, so that the length of the pendulum could be increased to give a period of 6 seconds. The pendulum with the short period could be altered from a period of 0·6 of a second to 2 seconds.

The bucket was loaded round the centre with lead shot, so as to make the total mass 40 grams when half filled with salt. The upper bob of the pendulum was made of a ball of plasticine, through which the wire was passed; the ball weighed 40 grams, and was placed three-quarters of the way from the suspension to the bucket. This, after slight adjustment, gave frequencies in the ratio 3 : 1.

Fig. 1.

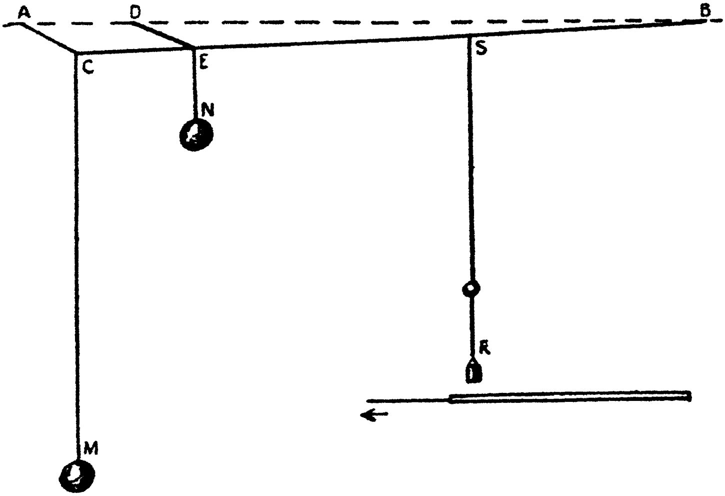
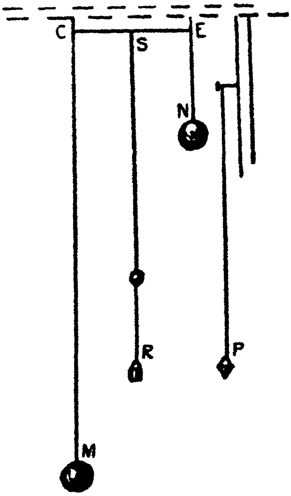


Fig. 2.



In order to obtain the ratio of the frequencies 2 : 1, the weight of the upper bob was made five times that of the lower, and it was placed in approximately the same position as above.

The loss of salt made it desirable to have the total weight of the bottom bob appreciable, or the alteration in the ratio of the periods during an experiment was very marked. It was calculated that for $p/q=3$, with mean $M=1$, for the bucket to start full of salt, and lose it all, the ratio of the periods changed from 2·7 to 3·3. It was found that during an experiment about one-third of the salt in the bucket was run out, so records were taken when the salt was running out from the middle, and this gave an alteration in the ratio of the frequencies of about 5 per cent. When the mean ratio of the frequencies was 2 : 1, the alteration during the experiment was about 2 per cent.

Calculations showed that the centre of gravity of the bucket, which, when full or empty, was at the geometrical centre of the bucket, was lowered by about one-tenth of the depth of the bucket when half empty. This lengthening of the longer component of the pendulum made about 2 per cent. difference in the ratio of the frequencies, but it could be arranged to make p/q slightly more constant.

At the side of the complex pendulum, about a foot away, a simple pendulum P, having a period equal to the longer period of the first pendulum, was fixed to a rigid support. This was made to oscillate in the same plane as the first pendulum, and a record of its motion was made by salt issuing from a small hole in the funnel which formed its bob. The record of its motion was used to check the periods of the complex pendulum.

Results.

In the photographic reproductions, the traces of the simple pendulum are always at the top, and since the motion of the board was from right to left, the traces start at the left and finish at the right.

In figs. 1 to 8 (Pl. XVI.) the ratio of the free vibrations of the complex pendulum was 3 : 1 approximately, the actual periods being 2·2 seconds and 0·715 of a second. In figs. 9 to 20 (Pl. XVII.) the ratio of the free vibrations of the complex pendulum was 2 : 1, the actual periods being 2·08 and 1·04 seconds.

Figs. 1 and 9 were obtained by keeping the driving pendulums still and allowing the driven one to oscillate with its own free periods. In both cases the motion was started by giving a blow to the upper bob. In fig. 1 it will be seen that the ratio of the vibrations is approximately 3 : 1, and in fig. 9 the ratio is about 2 : 1 ; but in neither case is the ratio quite constant, as is seen by the slight displacement of the kink towards the end of the trace. It has been explained earlier that it is difficult to eliminate this because of the alteration in the weight of the lower bob due to the loss of salt.

Figs. 2 to 8 are taken with the ratio of the periods of the responder as 3 : 1, and with the periods of the drivers also in the same ratio. The actual periods of the latter are changed; originally the long driver has a period less than that of the greater period of the responder, and, finally, the short driver has a period greater than the long period of the responder.

Table I. shows the actual periods of the driver corresponding with the figures on Pl. XVI. The periods of the responder are 2·2 seconds and ·727 of a second.

TABLE I.

No. of Figure.	Periods of Drivers.	Remarks.
1	None.	Responder started by blow to upper bob.
2	2·13 sec. and ·710 of a sec.	The two periods are seen distinctly.
3	2·15 sec. and ·707 of a sec.	
4	2·2 sec. and ·73 of a sec.	Trace unmanageable, due to resonance.
5	2·4 sec. and ·8 of a sec.	Only slight indication of shorter period.
6	5·85 sec. and 1·95 sec.	In 5, 6. and 7 beating due to free period of responder.
7	1st half 1·95 sec. 2nd half 5·85 sec. and 1·95 sec.	Traces show that the longer period has no effect.
8	5·85 sec. and 2·2 sec.	

If the ratio of the free periods of the responder is the same as that of the drivers, then about the point of resonance for the two vibrations the response is about equal for each. At any other point of resonance, the vibration due to one period only is apparent, this period being equal to one of the responder's periods.

Table II. gives the results with a responder of periods 2·08 and 1·04 seconds, that is, in the ratio 2 : 1. The drivers were in the ratio 3 : 1.

In all cases the damping of the responders is small; this prevents the driving pendulums from forcing their own periods on the responders. Thus, when the periods of the driver and the driven are the same, very strong resonance occurs. This may be seen from figs. 4, 12, and 15; but, when they are out of tune, it may happen that the responder will vibrate with its own free periods, and also those forced on it by the drivers. This is seen very

TABLE II.

No. of Figure.	Periods of Drivers.	Remarks.
9	None.	Responders started by blow to upper bob.
10	1·84 sec. and ·613 of a sec.	Free periods of responders very pronounced.
11	1·95 sec. and ·65 of a sec.	
12	2·08 sec. and ·69 of a sec.	Long-period driver in resonance with long-period responder.
13	2·40 sec. and ·80 of a sec.	Free periods of responders present.
14	1st half ·80 of a sec. only; 2nd half 2·40 sec. only.	In second half, beats due to free and forced vibrations.
15	3·12 sec. and 1·04 sec.	Short-period responder in resonance with short-period driver.
16	4·16 sec. and 1·39 sec.	Analysed by Harmonic Analyser—see below.
17	1st part 4·16 sec. only; 2nd 1·39 sec. added; last 1·39 sec. only.	Driver with long period has very small effect.
18	5·64 sec., 2·08 sec.	Short driver in resonance with responder of long period.
19	5·64 sec., 1·88 sec.	Shows beats due to responder having free period slightly different from that of one driver.
20	5·65 sec., 1·88 sec.	Made periods of responders 1·85 sec. and ·925 of a sec. Response due to short-period driver only.

strikingly in fig. 16. On examining the trace with the harmonic analyser, the following results were obtained :—

Period of Vibration.	Relative Amplitude.
4·16 sec.	33
2·08 „	100
1·39 „	73
1·04 „	28

The largest amplitude is shown as 100. Thus it is seen that the long free period is the most intense, and the short free period the least intense of the vibrations present.

These effects would no doubt be greatly reduced by damping the responding system, so that the free vibrations were only present for ten or twenty oscillations. However, as the work was undertaken to illustrate what would occur in a machine with free periods of its own, worked by external forces, it is probable that the photographic reproductions of the vibrations made by the pendulums is a good example of the type of motion of the electrical machine.

I should like to thank Mr. H. Cotton, M.B.E., M.Sc., A.M.I.E.E., for giving me some notes about the rotary-converter, on which he has been working, and for suggestions in connexion with this paper.

Nottingham.
Dec. 28, 1928.

LXXXVI. *On the Spectra of Alkali Metals excited by Active Nitrogen. By* J. OKUBO *and* H. HAMADA *(from the Laboratory of Physics, Sendai, Japan)* *.

[Plate XVIII.]

Introduction.

A PREVIOUS communication † on the results of an investigation of spectra emitted from various metallic vapours in contact with the stream of the active modification of nitrogen gas dealt primarily with the determination of the highest levels of the spectral terms which were excited by the gas. In the course of the experiments, as Lord Rayleigh and A. Fowler ‡ have already remarked, a very interesting phenomenon was observed in the case of sodium vapour. When metallic sodium is heated in the side bulb connected with the after-glow tube, a bright green light column is visible in the neck of the bulb where the dense vapour meets the stream of active nitrogen, and surrounding this column a broad yellow aureole diffuses in a large volume. Spectroscopic observation shows that the subordinate series appears with great intensity in the inner green column, while the principal series is strongly visible in the outer diffused aureole. It was remarked in our former paper that this difference in these colours depends absolutely on the density difference between the vapour in the central column and that in the outer aureole.

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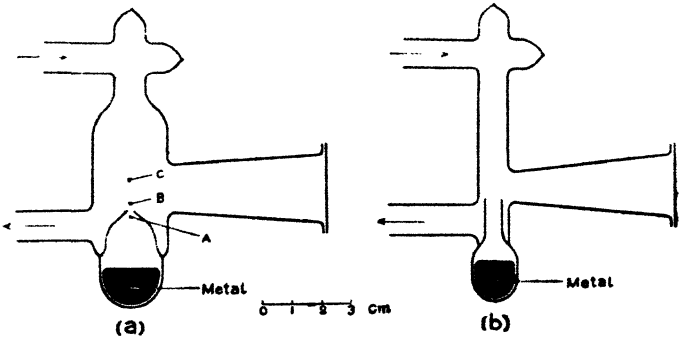
* Communicated by the Authors.

† J. Okubo and H. Hamada, Phil. Mag. v. p. 372 (1928).

‡ R. J Strutt and A. Fowler, Proc. Roy. Soc. lxxxvi. p. 105 (1912).

In this paper the results of further continued observation of the dependence of the spectral line on the density of the vapour of sodium are reported. It has also been confirmed that when a dense vapour of sodium is in contact with active nitrogen, the band spectrum due to the sodium molecules comes into view in addition to the line spectrum, and, on a further increase of the vapour density, an excitation of the band spectrum due probably to the sodium nitride results.

Fig. 1.



(a) (b)

A similar phenomenon was also observed in the case of vapours of both potassium and cæsium.

Experimental Arrangements.

In order to study the dependence of the spectral terms on the density of the vapour precisely, the following types of after-glow tube, as shown in fig. 1 (*a*) and (*b*), were used. Tube (*a*) is made of Pyrex glass, its diameter being 2·5 cm. and height about 10 cm. On heating the bottom of the tube, the vapour of the contained metal issues from the nozzle into the stream of the active nitrogen. The diameter of the nozzle was generally about 2 mm. It is possible to vary the pressure of the vapour at the nozzle and at any point in the tube by selecting a nozzle of a requisite diameter and adjusting the quantity of heat supplied.

The other parts of the apparatus, with the exception of the after-glow tube, were the same as those used in previous experiments. The spectrograph used was a quartz spectrograph of strong illumination made by C. A. Steinheil Söhne & Co., and the intensities of lines were measured with a Moll type of registering microphotometer.

The light-emissions from various parts of the after-glow tube, after passing through the quartz plate window of the a tube and quartz-fluorite achromatic lens, fall on the slit of the spectrograph. It is necessary here to measure the temperature of the vapour at various points of the tube, and a thermocouple of platinum and platinum-rhodium was put in at the points A, B, or C. Point A is 2 mm. below, B 2 mm. above, while C is 1 cm. above the nozzle. It was found that the temperatures of these points were not sensibly altered in spite of the flow of the activated or non-activated nitrogen gas, and it can be conceived that the temperature indicated is that of the vapour itself.

Experimental Results.

(1) *Sodium.*—By gradually heating the bulb with a small Bunsen flame and allowing the stream of the activated gas to flow continuously, a yellow glow begins to appear at the nozzle when the thermocouple indicates the temperatures 250° C. and 160° C. at A and B respectively. This glow gradually spreads out as the temperatures at A and B increase, and a greenish-yellow core appears at the stage when the temperature indication at B is 250° C. It should here be remarked that this greenish-yellow core is the intermediate stage leading on to the green core which is observed at the greater density of the vapour, and also that at this stage snow-like white compounds are deposited in a marked degree round the nozzle.

As shown in Pl. XVIII., *a* and the microphotogram (*e* in the same plate), the spectral lines observable from this yellow glow are lines belonging to the principal series; the D-lines are the strongest, the second member at λ 3302–03 Å. moderately intense, while the third member is so faint that it requires a very long time to photograph it. The lines of the subordinate series are weak.

Further, as the temperature of the bulb increases, a green core at the nozzle appears in the yellow diffused glow. One of the spectrograms obtained at this stage is reproduced at *b* in the annexed plate, at which the temperatures at A, B, and C were 360° C., 260° C., and 240° C., respectively; spectrogram *c* was obtained at the stage when the temperature of the bulb was higher and the green core more extended in volume. As the yellow aureole always surrounds the central green core, it is impossible to observe the light from the central core alone by using type (*a*) as the after-glow tube, and we have used another type as shown in fig. 1 (*b*), the diameter of which is 1 cm. and that of the nozzle 5 mm. One example of the spectrograms from this central core is reproduced in Pl. XVIII., *d*. On comparing record *d* with *a*, we see that there are remarkable differences between them. Firstly: in the green core the first subordinate series is more enhanced than the principal series, while in the case of the yellow aureole this effect is reversed. Further, the intensities of the lines of the former series are greater than those of the energy corresponding member lines of the latter series; and as the levels of energy become higher and higher, this fact becomes more and more conspicuous; *i.e.*, the lines of the first subordinate series come out clearly up to higher levels than those of the principal series on the photographic plate. Also, the lines of the second subordinate series appear up to the higher terms in the green core. The microphotometric study of the spectrogram also confirms this conclusion (Pl. XVIII., *f*). Secondly: in the green core the second member of the principal series is more intensely developed than the first member in the plate, and the third member appears moderately intense; in other words, on the plate the intensity maximum is displaced towards the higher member, while in the yellow aureole the intensities of the lines of this series decrease rapidly with the term number of the series. Thirdly: in the green core the green band spectrum is visually observable in the position lying between the lines $2p$–$4d$ and $2p$–$6d$. These bands are due beyond any question to the sodium molecules Na_2, though the red bands accompanying these green-blue bands are so faint that we failed to observe them. As is remarked in a later paragraph, an indigo-coloured new band system comes into view in the more dense vapour state of the green core. Lastly, it will be worth remarking that the deposit formed near the nozzle is dark grey in colour, and the amount of it is not so great as in the case of the yellow core.

The lines recorded in both plates after 5 hours' exposure, one observed through the yellow aureole and the other through the green core, are given in the following table. Under both conditions the lines of the higher members can also be observable on the plate with an exposure of many hours' duration :—

Obs. Lines.			
Yellow Aureole.	Green Core.	Class.	Energy.
5890–96	5890–96	$1s$–$2p$	2·09
3302–03	3302–03	$1s$–$3p$	3·74
	2853	$1s$–$4p$	4·33
	6161–54 to	$2p$–$3s$ to	4·09 to
	4423–20	$2p$–$7s$	4·88
5688-83	5688–83 to	$2p$–$4d$ to	4·26 to
	4216–13	$2p$–$12d$	5·02

(2) *Potassium.*—Similar phenomena were observed in the case of potassium and cæsium. In the case of potassium vapour, the outer diffused aureole is faint green and the dense central core is pink. In the outer aureole the principal series, $1s$–$3p$ and $1s$–$4p$, appears intense and the subordinate series lines are weak. On the other hand, in the pink core the subordinate series is more enhanced than in the case of the outer aureole. It is also noticeable that similarly as in the case of sodium, the lines at λ 3217–18 Å. and the higher lines of the principal series are relatively enhanced in the pink core.

(3) *Cæsium.*—Through the purple aureole we observed the lines belonging to the principal series, while those of the subordinate series were very faint, and in the yellowish-purple core the lines of the subordinate series were more enhanced than in the case of the outer aureole. Also, the relative enhancement of the higher members of the principal series, for example, λ 3612 Å. and λ 3477 Å., were observed in the central core, in which the decrease of intensity in the subordinate series lines with the term number is much smaller than in the case of the principal series, similarly to the former two cases. As regards the absence of the lines observed in the cæsium and recorded in the previous communication, they are given in the following table :—

Obs. Lines.	Class.	Obs. Lines.	Class.
4555	$1s$–$3p_1$	6973	$2p_1$-$5d_1$
4593	$1s$-$3p_2$	6723	$2p_2$-$5d_2$
3876	$1s$–$4p_1$	6213	$2p_1$–$6d_1$
3889	$1s$–$4p_2$	6010	$2p_2$–$6d_2$
3612	$1s$–$5p_1$	5845	$2p_1$-$7d_1$
3477	$1s$–$6p_1$	5664	$2p_2$-$7d_2$
		5635	$2p_1$–$8d_1$
6587	$2p_1$–$4s$	5466	$2p_2$–$8d_2$
6355	$2p_2$–$4s$		

(4) *The Band Spectrum.*—As we have already remarked, when the pressure of the sodium vapour near the nozzle is

sufficiently high, a band spectrum is observed in the central green core, as shown in Pl. XVIII., *b*, *c*, & *d*, and also in the microphotogram (*f*, in the same plate). Two bands are observed which have maxima of intensity at λ 4530 and λ 4364 Å.; the latter is more intense than the former, and they may probably be identified with the bands at λ 4541→4498 Å. and λ 4390→4340 Å., which R. W. Wood and R. H. Galt* have observed in the fluorescence spectra of the sodium vapour excited by cathode rays. It must be borne in mind that in their experiment a small quantity of air was mixed in the vapour as impurity.

Owing to the small dispersive power of our instrument, it was impossible to observe precisely the structure of the band, and so any definite conclusions deduced regarding the origin of the bands may be inadequate. But certainly it cannot be due to the sodium vapour itself, as no one has hitherto observed the bands in wave-lengths in these positions in any spectrogram of pure sodium vapour; so they will probably be due to the molecules of sodium nitride, and a further investigation of the structure and the origin of these bands is desirable.

Interpretation of the Results.

The intensity of a spectral line depends mainly on two factors: (1) the concentration of the initial energy level of the atom; (2) the probability of the transition. The first factor depends on the external circumstances, but the probability of the transition is affected by these circumstances to a very small extent, and it may be regarded as the true atomic reality. The experimental results just described, regarding the intensity difference between the spectral lines in the yellow aureole and in the green core, in the case of sodium vapour, can be accounted for by taking into account the collisions of the second kind between excited atoms and neutral ones, and also the conclusions which were deduced by H. Bartels † from his experiments on the vacuum arc in sodium vapour; *i.e.*, the transitions allowed by the selection principle of the azimuthal quantum number are highly favoured in the excitation process by electronic collision. As the results are very clearly observable in the case of sodium, it is convenient to discuss the question in relation to this case, and apply our conclusions similarly to the cases of potassium and cæsium vapours.

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* R. W. Wood and R. H. Galt, Astrophys. Journ. xxxiii. p. 72 (1911).

† H. Bartels, *Zeits. f. Phys.* xxv. p. 378 (1924).

From the experimental result that, in the yellow aureole, the higher member lines in the principal series are much weaker than the lower member lines in comparison with the corresponding result in the usual cases of excitation, while the lines of the subordinate series are very faint, it will be conceived that the concentration of atoms to the states of lower levels is much greater than that to those of higher levels of energy, in comparison with that in the usual cases of excitation. As the energy available is sufficient to excite the higher levels, this interesting distinction is due entirely to the characteristic of the triple collisions. In the aureole, where the density of the sodium vapour is comparatively small, the electrons of the sodium atoms are initially in the 1*s*-levels, and are excited to the *p*-levels by receiving the energy from the activated gas, the line emissions of the principal series being thus caused.

In contrast with the case of the yellow aureole, the subordinate series in the green core is much more enhanced than the principal series, and there is another peculiarity, viz. that the second member of the principal series is more brightly developed than the first member, while the third member is also enhanced. It is to be considered that in this green core the sodium atoms are in the excited states of the 2*p*-levels, and the electrons are lifted to the higher levels by receiving energy from the activated gas, the line emissions corresponding to greater energy of excitation being thus caused. The reason why the considerable part of the sodium atoms in the green core is in the states of the 2*p*-levels may be explained if we consider the process of the collision of the second kind. Obviously, the electrons, at first, are excited to the 2*p*-levels as in the case of the yellow aureole, and there will be three possible causes of the concentration of the atoms in these excited states: namely (1) through the unexcited atoms absorbing the energy of the D-radiation, (2) through the activated gas colliding with many sodium atoms and exciting them to these levels, (3) through the exciting atoms colliding with other unexcited atoms, and, the energy being transferred from one to the other, the energy being reserved in the sodium atoms for a comparatively long duration. But there is no reason why the first and the second processes should be more favoured in the core than in the aureole, while the third process is much the more likely one in virtue of the greater density of the atoms in the core, and there must be many chances of radiationless transferences of energy occurring among the sodium atoms. And therefore the large concentration of the excited atoms in the states of $2p$-levels is certainly due to the collisions of the second kind. The weak appearances of the D-lines will also be explained as the consequence of conserving the $2p$-levels in the atoms.

The second excitation process to the higher levels from the $2p$-levels is to be considered as entirely due to the direct collision between the activated gas and the excited atom. It is clear that atoms present in the states of the $2p$-levels are no longer in a condition to absorb the D-radiation, and, assuming a collision between two atoms in the states of the $2p$-levels, it is difficult to explain the line emissions corresponding to a higher excitation energy than 4·18 volts. We must therefore conclude that the energy-lifting of the electron to the higher levels comes directly from the active nitrogen.

As the greater part of the atoms is lifted to states of higher levels from the $2p$-levels upwards, the enhancement of the subordinate series is clearly conceivable in the core, and the energy by which the electron is excited to the higher p-levels from the normal level is greater than that by which it is excited to the s- or d-levels of the energy corresponding member lines from the $2p$-levels upwards; it therefore follows that the higher terms of the subordinate series are more enhanced under these circumstances than those of the principal series. In this case the secondary transitions to the $3p$-levels from the higher s- or d-levels occur in addition to the primary transitions to the $3p$-levels from the $1s$-level, and we can understand why the second member of the principal series appears brightly. It may also be considered that the line emissions of the higher members of the latter series are mainly due to these secondary transitions.

As described above, all the results obtained in this experiment can be satisfactorily explained by taking into account the effects of the collisions of the second kind and that of the azimuthal selection principle in the excitation process by the active nitrogen. The phenomena described in this communication can only be observed in the case of the alkali metals, but not in the case of other metals.

In conclusion, the present writers express their best thanks to the Saito Gratitude Foundation for the expenses of this experiment, which were paid by the Research Fund from the Foundation.

Sendai, Japan.
October 1928.

LXXXVII. *Note on Superposed X-Radiations. J-Phenomenon* (Part IX.). *By* C. G. Barkla, *F.R.S., and* M. M. Sen Gupta, *Ph.D., University of Edinburgh*[*].

It was shown by Barkla and Miss Mackenzie that the superposition of a beam of Röntgen Radiation (Y) on another beam (X) changed the properties of that beam X; that X and Y proceeding together from neighbouring sources behaved, as far as the J-Phenomenon was concerned, as a radiation with properties of its own distinct from that of X or Y; that the J-discontinuity for the beam X+Y was in the position not appropriate to either of the constituent beams X or Y, but in a position between these and appropriate to the radiation X+Y as a whole.

In the experiments referred to above, the two radiations X and Y were radiations scattered from neighbouring scattering plates, they were propagated together in the same direction, through the same absorbing sheets into the same testing ionization chamber. The feature which was observed was the J-discontinuity in the absorption in aluminium as an increasing thickness was placed in the path of the radiation to the ionization chamber. The critical thickness of aluminium at which the discontinuity occurred was equally dependent upon the original and the superposed radiations—indeed each constituent radiation made only its contribution to some kind of average, analogous to temperature, which controlled the phenomenon. It was this property of "coherence" of superposed X-radiations which we decided to investigate further, and to study under even simpler conditions than previously. For, as stated, the beam Y was superposed on the original beam X from its source, through the intervening air and the absorbing aluminium, and finally across the ionization chamber used to measure the intensity. Though other experiments had shown that the critical state was produced in the absorbing sheets of aluminium, for the discontinuity was characteristic of that substance, it seemed advisable to limit the superposition to that produced in the absorbing substance alone, and, in particular, to avoid superposition in the ionization vessel. In the experiments described below, therefore, the two superposed beams X and Y had their origin in two widely separated scatterers; they proceeded in directions making an angle of approximately 45° with one another; they crossed the absorbing sheets and separated again so that the ionization produced by the beam

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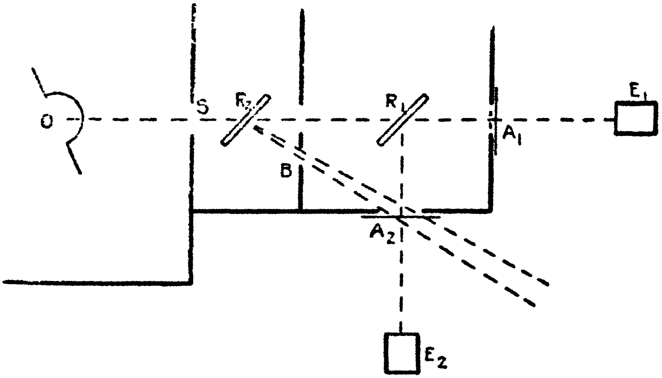
[*] Communicated by the Authors.

X was studied quite independently of that produced by the beam Y. Superposition thus occurred only in and immediately around the absorbing aluminium. As will be seen below, the two beams were still "coherent"; the transmission of the beam Y through the absorbing aluminium affected the absorption of the beam X.

Preliminary experiments were made under conditions very similar to those of the experiments of Barkla and Miss Mackenzie. In our experiments, however, the scattering substance was paraffin-wax or paper instead of aluminium, and the scattered radiation studied was that proceeding in a direction approximately at right angles to that of propagation of the primary radiation. The discontinuities again occurred in positions appropriate to the beam as a whole, and were displaced by the superposition of other radiations. The results agreed in all essential features with those of Barkla and Miss Mackenzie.

Fig. 1.



Experimental Arrangements.

The simplifications of conditions which we proposed was effected in the following way :—

The arrangement of apparatus is shown in figs. 1 and 2 in which most of the lines represent lead screens. Slabs of paraffin-wax were placed in positions R_1 and R_2, so that when the lead shutter at the aperture S was removed, they were both exposed to the primary radiation from the Coolidge Tube O. In one case (fig. 1), R_2 was traversed by the primary radiation before its incidence on R_1. In the other case, R_2 was exposed to the primary radiation after transmission through the radiation R_1. Thus in the former case, the heterogeneous radiation scattered from R_2 was on the average "softer" than that from R_1; whereas in the other case the radiation from R_2 was "harder" than that from R_1. Apertures in the lead screens permitted the secondary radiations from R_1 to pass directly into the ionization chamber E_2, and that from the radiator R_2 to cross its path by means of the aperture B. Consequently, it was necessary only to remove a lead screen from aperture B in order to superpose the radiation from R_2 on that from R_1 as it traversed the absorbing sheets at A_2. Thus the absorption of the radiation from R_1 was compared under the two conditions—(1) without and (2) with the radiation from R_2 passing through the absorbing sheets. The method of procedure was to observe the ratio of ionizations produced by the secondary and primary radiations in the ionization chambers E_2 and E_1. Let this ratio be S/P. Similar sheets of aluminium were placed across the apertures A_1 and A_2, and the ratio S′/P′ of ionizations produced by the transmitted radiations was again determined. As this was done for increasing thicknesses of aluminium, the ratio S′/P′ suddenly dropped, when the critical condition for the scattered radiation was reached. When, however, the scattered radiation from R_2 was allowed to cross the absorbing aluminium, the discontinuity in the absorption of the radiation from R_1 occurred at a different point, that is, for a different thickness of the absorbing sheets. Also the displacement of the discontinuity was invariably in that direction which was found when the superposed beam was a constituent part of the radiation, the absorption of which was being tested. Thus with the arrangement of radiators shown in fig. 1, when the radiation from R_2 was prevented from falling on the absorbing aluminium at A_2 the J-discontinuity in the absorption of the radiation from R_1 occurred for a thickness of aluminium between ·03 and ·04 cm. Whereas, when the absorber was traversed by the radiation from R_2 the discontinuity in the absorption of the R_1 radiation occurred at a thickness between ·05 and ·06 cm. (See fig. 3, experiment 1.) In this case the superposed radiation (from R_2) was "softer" than the radiation experimented upon, consequently the whole atmosphere of radiation in the absorbing substance was "softer" than when the absorbed radiation was alone. The absorbed radiation had thus to traverse a greater thickness of absorbing aluminium before the average absorbability reached the critical value.

With the other arrangement of radiators, shown in fig. 2, the superposed radiation from R_2 was of more penetrating type than that of the radiation from R_1 ; consequently, the superposition of the R_2 radiation made the whole atmosphere of the radiation traversing the absorbing aluminium, on the average, of more penetrating type. Hence, a smaller thickness of absorbing aluminium was necessary to bring the average absorbability to the critical point. In this case,

Fig. 2.

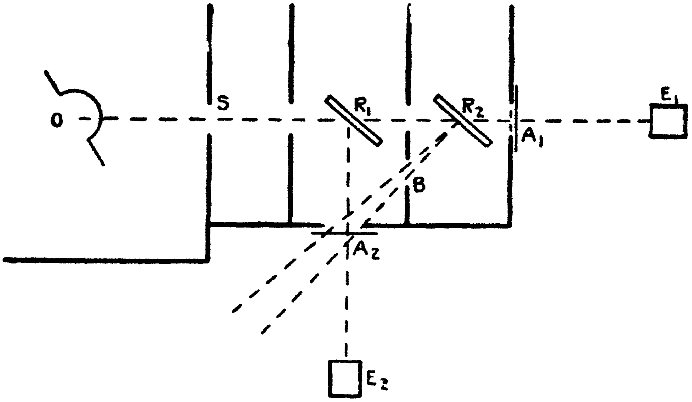
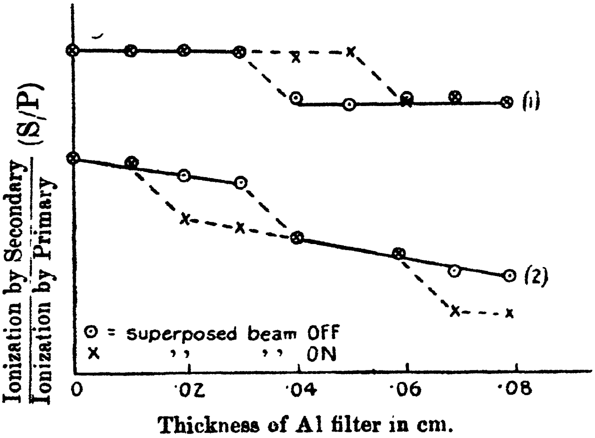


Fig. 3.



Case 1=superposed radiation of lower average frequency.
Case 2= " " of higher " "
Showing displacement of J-discontinuity by a second radiation.

then, the superposition of the R_2 radiation displaced the J-absorption discontinuity in the reverse direction, *i. e.* to the left of fig. 3.

These results are exhibited graphically in fig. 3, Exper. 2. The horizontality of the lines in fig. 3, Exper. 1, illustrates again the equal absorptions of scattered and primary radiations away from the discontinuity. The gradient in Exper. 2 indicates, of course, greater absorption of the scattered radiation, as was to be expected when the scattered radiation studied was that from the *front* face of the scattering sheet. This was of no significance in our experiments; the position of the discontinuity was the feature under observation, and this was as clearly marked in one case as in the other.

It is important to notice that, except for the discontinuity, the absorption of the scattered radiation was precisely the same whether the radiation from R_2 was "on" or "off," *i. e.*, the absorption of the radiation from R_1 was not affected by the superposed radiation. This is shown by the positions of the circles and crosses away from the discontinuity; they are superposed in fig. 3.

The question naturally arises, does the discontinuity—that is the sudden diminution in ionization *—indicate true absorption? To give all the evidence on the subject would require a separate paper, but sufficient has already been indicated in previous communications. It is the sudden occurrence of a process which, under other conditions, may be made more gradual and which is then generally recognized as absorption—indeed, it cannot be anything but absorption as the term is generally understood.

Thus the absorption of a given radiation, when the condition is neighbouring on a J-discontinuity, is dependent on other radiations traversing the absorbing substance. In other words, the absorbing property of aluminium (and presumably of other substances) depends not merely upon the radiation, the absorption of which is being measured, but upon the whole atmosphere of radiation traversing that absorbing substance. And thus again we have shown that the processes taking place in matter traversed by radiation depend upon a "coherence" of the various constituents of that radiation—a coherence, that is, in the sense that the constituents *combine* to produce an absorbing state in the matter itself. As far as we have seen, every constituent in the radiation affects the absorption of the other constituents; the radiation must be considered as a whole and not as a number of independent parts. To what extent, either in space or time, this coherence is effective is a matter for further experiment. It will be interesting to determine whether such a coherence can be established between the radiations from two entirely independent sources. In our experiments the two radiations superposed must necessarily have been very similar in structure, for they were the radiations scattered from the same primary beam in transmission through substances of the same constitution. Whether or not the radiations scattered by (*a*) *dissimilar* substances from the *same* primary beam, or (*b*) *similar* substances in *different* primary beams, or even by (*c*) two *similar* substances in the *same* primary radiation, but widely separated so as to produce a very large difference of path, would have "cohered" it is impossible to say without further investigation. Such experiments as have been made by superposing γ-rays upon X-rays have indicated the complete independence of the two; but we are not yet prepared to say that coherence does not occur under favourable conditions. For the present, the intimate relation between two radiations traversing matter at the same time is the important thing; indicating, as it does, that all the constituents in the atmosphere of radiation are contributing to the state of the matter which controls absorption—at least that portion of it which we have called the J-absorption.

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* The "step" was about 7·5 per cent. of the total ionization measured.

LXXXVIII. *Chromium Echelette Gratings on Optical Flats for Infra-red Investigations.* *By* R. W. Wood *.

[Plate XIX.]

ECHELETTE gratings were first described in the Phil. Mag. for Oct. 1910. They were ruled with an hexagonal carborundum crystal, mounted, as shown by a figure illustrating the paper, on plates of polished copper as supplied for the half-tone process of photo-engraving. The surfaces of these plates had a very poor "figure," of course, and the gratings could not be used for precision work. In spite of this, however, the author, in collaboration with Professor A. Trowbridge (Phil. Mag. Nov. 1910), resolved the CO_2 band into a doublet with maxima at $4{\cdot}3\mu$ and $4{\cdot}43\mu$. This was two years before Bjerrum predicted the doublet structure of vibration-rotation bands (also foreseen by Lord Rayleigh as long ago as 1892), the experimental verification of the theory being usually attributed to Burmeister (*Ver. deut. phys. Ges.* xv.

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* Communicated by the Author.

p. 589, 1913) and Eva v. Bahr (for CO) (*Ver. deut. phys. Ges.* xv. p. 710). As a matter of fact, the experimental proof of the Rayleigh-Bjerrum theory was already accomplished two years before the appearance of Bjerrum's paper. The theoretical importance of the observation was, of course, not realized at the time, and the paper was published under the title "Notes on Infra-red Investigations with the Echelette Grating." It is therefore not surprising that the matter was overlooked.

The recent increase in the field of research in infra-red spectroscopy, resulting from the development of the theory of molecular band spectra, has made it appear worth while to improve this type of grating. As is well known, very excellent results have already been obtained with echelettes ruled on aluminium at the University of Michigan.

It was found that carborundum crystals were too fragile to be depended upon, but excellent results were obtained, with a diamond ground and polished to the proper angle, on optical flats of copper plated with gold. The Hilger Company furnished the plates with which the first of the new experiments were made, and some very fine echelettes were ruled on the old Rowland engine. A photograph of one of these with 2060 lines to the inch is reproduced (Pl. XIX.) standing upright on its printed label. It throws nearly all of the energy into the eighth order for mercury green light, and the reflexion of the printed characters on the label appears in an oblique direction (in the ruled portion) in the spectrum of this order. This grating would give a first-order spectrum in the same direction for radiations of wave-length 4·3 μ.

It seems probable, however, that the gilded gratings may not prove very durable in the presence of mercury vapour, and experiments were accordingly undertaken to see whether a surface of chromium could be used. The gold gratings were plated before the ruling, as with a properly-mounted diamond no metal is removed during the ruling, the grooves being pressed into the material. This method could not be employed in the case of chromium plating, owing to the excessive wear of the diamond on the very hard metal. It was found, however, that the chromium could be deposited electrolytically, after the ruling had been accomplished, without changing in the slightest degree the distribution of the light. Gratings of this description on disks of copper 4 inches in diameter and ¾ of an inch in thickness can now be supplied to any laboratories desiring them. They can be ruled for concentration at any desired wave-length range (expressed in μ) and with any desired spacing, though we choose the spacing according to the region to be investigated.

Some very good concave echelettes of 1 and 2 metres radius have also been made which resolved the CO_2 band easily, but it is believed that plane gratings will prove more satisfactory, as they can be used with long-focus mirrors for high resolution and with short-focus ones for intensity. A collection of three or four, ruled for concentration in different spectral regions, is desirable. The 4-inch gratings are priced at $100 each.

The ruling of 5-inch disks will be commenced very shortly.

Johns Hopkins University,
Baltimore, Md., U.S.A.

LXXXIX. *The Raman Effect in Gases.*—Part I. *HCl and NH_3.* *By* R. W. Wood[*].

[Plate XX.]

As mentioned in a letter to 'Nature' of Feb. 2, spectrograms have been obtained of the lines of modified wave-length in the light of the mercury arc scattered by a gas at atmospheric pressure. A very special technique is required, on account of the weakness of the light; nevertheless, records have been secured with an exposure of only five hours with an F 2 one-prism spectrograph, by employing the apparatus to be described presently. With HCl a very surprising result was obtained, namely: for each exciting line a single line only, of modified wave-length, was radiated, and the frequency difference between the exciting and emitted radiation was the frequency of the "missing line" of the infra-red absorption band at 3·4645 μ. The spectrogram from which this determination was made was a Bausch and Lomb constant deviation spectroscope, the camera lens having a focus of 50 cm.

The three prime requisites for obtaining the effect with gases at atmospheric pressure are: very intense illumination of a long column of gas, an absolutely black background, and complete absence of scattered light from the front window. The last condition is the most important and the most difficult to fulfil.

The apparatus employed is shown in fig. 1. It consists of a tube of soft glass 5 cm. in diameter and about 150 cm. in length, drawn off into a tapering cone at the rear, and constricted and expanded at the front as shown in the diagram.

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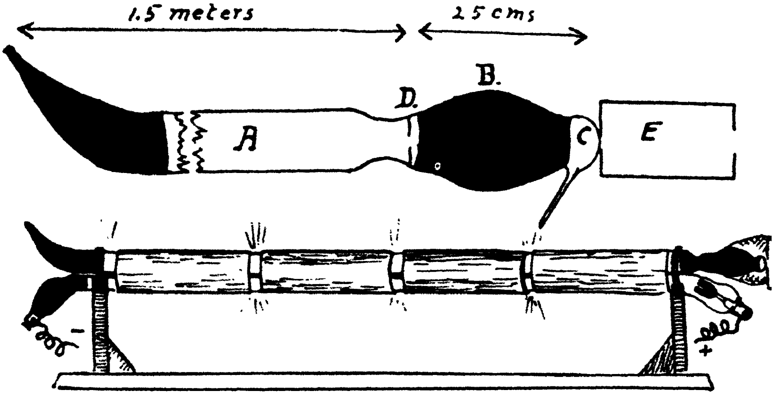
[*] Communicated by the Author.

The lower figure is drawn more nearly to scale, and shows the tube mounted over, and in contact with, a very long Cooper-Hewitt mercury arc lamp of glass. Hollow cylindrical reflectors of very thin highly polished sheet aluminium enclose the two tubes, shutting in all of the light. This is a great improvement on the earlier "light furnaces" described in former papers on iodine fluorescence.

The cylinders were made by wrapping rectangular sheets of the metal around a glass tube of much smaller diameter than that desired, a size being chosen such that the edges of the sheet remained in contact when it expanded by its elasticity.

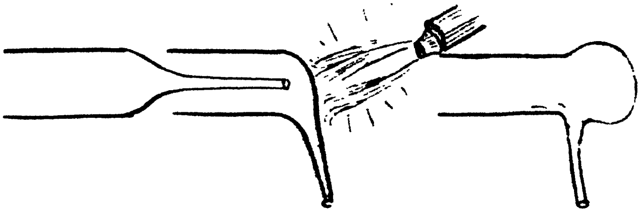
The cylinders are slipped over the tubes by springing them open with the fingers, and on releasing them they clamp themselves firmly around the two tubes. The upper diagram is not drawn to scale. The bulb B is rather longer in proportion to its diameter than is indicated in the figure. This bulb prevents reflexion of light coming from the mirrors and lamp through the diaphragm D, against the front wall of the bulb C. The preparation of this latter bulb is the most important part of the whole operation. It must be as thin as possible and optically clean, *i.e.*, free from air-bubbles, striæ, or cloudiness. The front wall should not be thicker than thin writing-paper, and if properly made gives almost as clear vision down the tube as a plate-glass window. A window of thin cover glass could be cemented on, in the case of most gases, but I preferred the bulb for the work with HCl.

Fig. 1.



The diaphragm D is a disk of very thin platinum foil, perforated by a hole 4 mm. in diameter, which is as large as can be safely used, as the condition which must be fulfilled is that *no part* of the lens used for projecting an image of diaphragm on the slit, can "see" any part of the blazing interior of the furnace through the diaphragm. The platinum disk is dropped into position resting against the sloping wall of the constriction (the tube being held vertically), and the glass then melted in spots with a small pointed blast-lamp flame until it takes hold of the platinum. The bulb B is then blown, drawing it out during the blowing, and finally the end bulb and exit tube prepared. The three stages of this process are shown in fig. 2. The tube is first drawn down, and bent at a sharp right angle as shown, the narrow tube being about 20 cm. long, however, so that it can be used for blowing the bulb. The flame is then directed against the flattened end and the bulb blown to paper thickness. It is wise to practise blowing these thin bulbs on some scrap pieces of tubing of the same size, before

Fig. 2.



making the long tube. The tapering cone and the large bulb are now painted black on the outside. "Duco" auto-enamel paint will answer, but an asphaltum paint is slightly blacker and preferable for the cone.

E is a cardboard mailing cylinder covered with black paper at each end perforated with small holes as shown. This is to screen the front surface of the bulb from light from the walls of the room and neighbouring objects. After mounting it in place, a piece of black cloth is wrapped around the bulb and cylinder as shown in the lower figure. This prevents light escaping from the end of the "furnace" from reaching the black paper and being in turn reflected against the front bulb wall. The room is dark except for the light which escapes from the furnace.

The tube was filled with dry HCl, the gas being introduced through the cone end, with the tube in a vertical position, and the exit tube close to an open window with an outward draught. Small samples of the escaping air were taken in a test-tube from time to time to determine when the gas had reached the top. The ends of the tube were then sealed with a flame. Notwithstanding the circumstance that the tube had been heated and ventilated with dry air for some time previous to filling it with gas passed over calcium chloride and phosphorus pentoxide, it showed a marked "fog" when illuminated in the furnace. After standing overnight, however, it cleared up and gave no further trouble. The gas was prepared by dropping concentrated sulphuric acid into a flask containing hydrochloric acid, through a funnel tube which dipped below the surface of the acid. The sulphuric acid was fed into the funnel at the rate of about one small drop every three seconds by means of a second funnel drawn down to a capillary.

The Cooper-Hewitt lamp was mounted on two thin wooden supports in V-shaped notches lined with asbestos board, and the gas-tube held down in contact with it by thin metal bands screwed to the supports and passing over the tubes.

The illumination produced in this way is terrific as the light of the lamp is beaten back and forth between the walls of the reflectors, and, as I have said, it was possible to photograph the modified line with a five-hour exposure, while the unmodified line comes out with an exposure of only 15 seconds, some of the light in this case coming undoubtedly from the "black cone" and the front wall of the bulb.

The proper aiming of the spectrograph is very important, a matter concerning which too little has been written. In the present case the best method is the following. We bring the eye in line with the two holes in the pasteboard cylinder, at a distance of about 1·5 metres from the end of the cylinder, and find the point from which we view the centre of the black cone at the far end of the tube through the platinum diaphragm. The edge of the circular aperture appears as a bright ring of light by diffraction. We now mark the position of the pupil of the eye by means of a match-stick held in a clamp stand, and moving the eye up and down and to the right and left, make sure that no direct light from the furnace walls will reach the lens which is to be mounted between the eye and the tube at a distance from the former equal to its focal length (with respect to the diaphragm).

The slit of the spectroscope is now brought up to the end of the match-stick, and the eye brought into the position to be occupied by the photographic plate. It may facilitate matters to place a "pea" electric lamp in front of the small hole in the black paper on the end of the cylinder. If the spot of light coming through the wide open slit is not at the centre of the field, the spectroscope must be turned accordingly, keeping the slit in coincidence with the marker, however. An achromatic lens (I used an F 4·5 Zeiss photographic objective of about 25 cm. focus) is now mounted in such a position as to form a sharp image of the hole in the platinum diaphragm on the slit, the approximate position being found with the "pea" lamp. It is of vital importance that a sharp image is obtained, otherwise the light diffracted by the edge of the aperture will ruin everything, for the mercury arc has a fairly strong continuous background.

We assure ourselves of this by getting a sharp image of the jaws of the slit (using a short-focus magnifier), and the bright circle of diffracted light at the same time, viewing them without a ground glass focusing screen of course. It is assumed that the spectrograph is properly focussed. The projecting lens is to be moved forward or back until the appearance of the wide open slit, seen by the light of the green line, is as shown by fig. 2 (Pl XX.), the two bright arcs being the upper and lower edges of the hole in the platinum disk shining by diffracted light while the luminosity between them comes from the gas.

Fig. 1 (Pl. XX.) shows the line of modified wave-length scattered by dry hydrochloric acid gas at atmospheric pressure. It falls nearly midway between the mercury lines 4358 and 4915 almost in coincidence with the argon line 4579·5, and its wave-length as determined from a plate made with higher dispersion than the one reproduced is 4581·8.

This line is excited by the mercury line 4046. The corresponding line excited by 4358 was recorded on one plate made with the F2 short-focus spectrograph, but it was very faint as it fell in a region of low sensitivity. The frequency difference between Hg 4046 and the HCl line corresponds to wave-length 3·466 μ in the infra-red.

Now this is almost exactly the wave-length of the "missing line," or the centre of the gap between the two branches of the absorption band as resolved and measured by Imes. The Raman line in this case does not identify itself with an absorption line, but does identify itself with a Q branch (vibration without rotation change) not observed in absorption. Professor Kemble has calculated that the "missing line" should have a wave-length of 3·4649 μ, and the Q branch 3·4689 μ. My value of 3·466 is in very fair agreement with this calculation. I have not yet found an explanation for the circumstance that on my first plates I found two lines, as reported in 'Nature.' One of these was the line 4581·8 (which we have been discussing), and the other was of slightly greater wave-length. The tube in this case contained a trace of water-vapour, and with a fresh filling with dry gas the single only has appeared. Experiments will be continued with this gas excited under varying conditions of temperature and with water-vapour, and other impurities, mixed with it. I hope to be able also to make still more accurate determinations of its mean wave-length and width, for it is distinctly wider than the argon comparison lines.

There are also a number of nearly equidistant bands close to the 4358 mercury line, which I at first thought might be interference maxima due to the passage of the light of the faint continuous spectrum through the very thin wall of the glass bulb, but I am now not sure but what they are real. If excited by the 4358 line, they might be identified with the rotation bands found by Czerny (*Zeit. f. Phys.* xxxiv.) between 40 and 100 μ.

The infra-red wave-lengths corresponding to these bands were calculated and found to agree fairly well with the *alternate* lines found in absorption by Czerny, as follows :—

Czerny.	Wood.
44·1	43·6
48·5	—
53·8	53·9
60·4	—
68·9	67·1
80·4	—
96	90 (Uncertain).

It is not worth while, however, to discuss them seriously until they have been obtained with a new tube having a bulb with a thicker wall.

Ammonia at atmospheric pressure gave a single line also, for each exciting line. A very sharp triplet excited by Hg 3650, 3654, and 3663, of which the outer lines had wave-lengths of 4157 and 4172. The 4046 line excited a line of wave-length 4672·5. Thus far I have photographed these with the F2 spectrograph only, and the wave-lengths are not very accurate. These lines are identified with the infra-red absorption band at 3 μ.

The ammonia was taken from a commercial iron cylinder and not purified. Coblentz gives this band at 3 μ and it is Band II. of Sir Robert Robertson's recent paper (Proc. R. S. 784, p. 161). No trace of lines corresponding to the strong ammonia bands at 6·5 μ and 10 μ have been observed as yet.

XC. *Notices respecting New Books.*

Beyond the Electron. By Sir J. J. THOMSON, O.M., F.R.S. (Cambridge University Press. Price 2*s*. 6*d*. net.)

THE recent experiments of Prof. G. P. Thomson on the passage of cathode rays through thin films of metals have furnished a remarkable verification of the de Broglie theory of electron waves.

These researches form the starting-point of the lecture on the structure of the electron and its surroundings. The electron is accompanied by a train of waves of very high frequency; the theory, on the basis of "Classical Mechanics," is set out in a supplementary note and the author shows that, between the wave-length and velocity of the electron waves, the same relation holds as for light-waves in a superdispersive medium, that the energy of the electron is proportional to the frequency, and the product of momentum and wave-length is constant. The new fields of research opened up by the experiments of G. P. Thomson, Rupp and Davisson and his co-workers will throw further light on the structure and properties of the electron.

Theory and Application of Infinite Series. By Dr. KONRAD KNOPP. (Translated from the second German edition by Miss R. C. YOUNG, L. ès Sc.) (Blackie and Son, Ltd. Price 30*s*. net.)

THE translation of Prof. Knopp's 'Theorie und Anwendung der unendlichen Reihen' deserves the favourable reception accorded to the first and second German editions, and thanks are due to the publishers for placing this translation in the hands of English readers. Private students in particular will fully recognise the debt they owe to the author for his useful and comprehensive work.

The first two chapters deal with real numbers and sequences, followed by several sections on series of positive terms, power series, infinite products, and series of complex terms. The section on divergent series has been considerably extended and sets out much of the recent work on this subject. The chapter on Euler's summation formula and asymptotic expansions has been specially written for the English edition and gives a review of the work of Stieltjes on asymptotic series, particularly in their application to the calculation of functions, *e.g.*, the exponential integral with both positive and negative argument. The very large number of practical exercises form a valuable feature of the book.

The Spectroscopy of the Extreme Ultra-violet. By THEODORE LYMAN. (Second edition. Longmans, Green & Co. Price 10*s*. 6*d*. net.)

WHEN the first edition of this book appeared some fourteen years ago Prof. Lyman had investigated the Schumann region as far as λ 900, and, two or three years later, to λ 500. In this second edition the author has incorporated some of the notable results in the region of still smaller wave-lengths, in particular, Millikan's work with the hot spark, first described by R. W. Wood thirty years ago, bringing the limit near λ 140. From the region of the soft X-rays, Dauvillier and others have obtained radiations of wave-length near Millikan's limit, with the consequent removal of the gap between optical spectra and X-rays. In the chapter on Emission spectra, the author has made available a mass of information on the spectra of a large number of gases and solids in the extreme ultra-violet. In addition to the tables of wave-lengths of the spectra of hydrogen and other elements, there is a bibliography of papers which have mostly appeared since the publication of the first edition of Prof. Lyman's book.

The Discovery of the Rare Gases. By MORRIS W. TRAVERS, D.Sc., F.R.S. [Pp. vii + 128, with frontispiece and 21 figures.] (London: Edward Arnold & Co. 1928. Price 15*s*. net.)

PROF. TRAVERS, in the course of arranging, at the request of Lady Ramsay, the scientific papers of the late Sir William Ramsay, came across a complete series of laboratory notebooks. Many of these contained little more than numerical data with brief descriptive notes, but with the commencement of the work which led to the discovery of argon, experiments were described in detail and drawings of apparatus given.

The original intention of Prof. Travers was to annotate and summarize these for the benefit of the future historian of the chemistry of recent years. This project was expanded until a manuscript volume giving an account of the discovery of the rare gases had been prepared. Friends and colleagues to whom the manuscript was shown insisted that it should be published.

Based as it is upon Sir William Ramsay's own notebooks and written by one who assisted in a large portion of the investigations described, the accuracy of the account can be relied upon. The successive stages of the long series of investigations, the first-fruits of which were the discovery of argon, and which led to the discovery, in order, of helium, krypton, neon, and xenon, are recounted. There were many difficulties to be faced; not only the difficulties inherent in the research itself but also difficulties arising from lack of funds for the purchase of apparatus and difficulties in obtaining the liquid air and hydrogen required. Liquid hydrogen was finally obtained from an extemporised plant constructed by Prof. Travers himself, and this enabled the investigations to be brought to a successful conclusion.

The two guiding principles to which Sir William Ramsay firmly adhered, in the face of much opposition, and which crowned these investigations with success, were: (i.) that a ratio of 1·67 for the specific heats of a gas is indication that the gas is monatomic; (ii.) the new gases had to fit in a proper manner into the periodic system of the classification of the elements.

The volume is illustrated with diagrams of apparatus and reproductions of pages from the original notebooks.

Old Mother Earth. By KIRTLEY F. MATHER. [Pp. xiv+177, with 61 illustrations.] (Cambridge: Harvard University Press. London: Oxford University Press. 1928. Price 11*s*. 6*d*. net.)

DURING the winter of 1927–28, the author was asked to give a series of broadcast talks at Boston dealing with the past history of the Earth. These talks, somewhat modified, are published in the volume under review. The author deals with the origin of the Earth, the origin of life, the evolution of mankind, the great ice-age, the formation of coast lines, earthquakes, and the formation of mountains. He has the gift of popular exposition; technicalities are avoided, but not at the expense of accuracy. The volume can be recommended to all who wish to know something of how the Earth, as we know it at present, has come into being. The arguments are illustrated by means of various geological features of New England, and the volume is therefore of greater interest to an American than to an English reader. The illustrations are numerous and good.

Bibliography of Crystal Structure. By J. K. MORSE. [Pp. xix+164.] (Chicago: University of Chicago Press. London: Cambridge University Press. 1928. Price 15*s*. net.)

THIS publication is issued by the Crystal Structure Laboratory of the University of Chicago, which was started in 1926. Part I. contains an account of the present work of the Laboratory, an outline of its development programme, and reprints of the papers on the crystal and molecular structure of organic and inorganic compounds which have been published from the Laboratory. The bibliography of crystal structure, including the related topics of atomic dimensions and molecular structure, forms the second part of the volume. The bibliography is arranged alphabetically by authors under each year from 1912 to 1927, and contains about 1800 entries, emphasizing the wide interest of this branch of research. The bibliography should prove of great value for purposes of reference.

XCI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 424.]

December 5th, 1928.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Erratic Rocks and the Age of the Southern Limit of Glaciation in the Oxford District.' By Kenneth Stuart Sandford, M.A., D.Ph., F.G.S.

The Plateau Drift around Oxford contains rocks brought from long distances:—from Scandinavia, Scotland, East Anglia, the Midlands, and, most surprising of all, from Devon and Cornwall. Excepting smaller pebbles, much of the material is subangular and some of it glacially striated.

The Drift entered the district through the Cotswold escarpment by gaps which the northern tributaries of the Upper Thames occupy, and it is found on their sides to a height of more than 600 feet above sea-level. There is no evidence of glacial erosion of the district within the scarp, though a few patches of Drift are recognized as Boulder Clay. The Drift is the homologue of the thick Boulder Clay which is still preserved outside the scarp; it was introduced either by a 'fluvio-glacial' inundation or during submergence, and was spread over the surface to the height stated irrespective of the old topographic features.

It is not suggested that heavy glacier-ice was the vehicle in every instance: for example, the material from the South-West was most probably carried on detached shore-ice drifting up the Bristol Channel. It is the presence of this material in the district which lends support to the view that the Southern Midlands in particular were submerged to a considerable depth.

The material, however introduced, was 'graded'[1] or redeposited in terraces up to 350 feet above the recent rivers, this process being subsequent to, and distinct from, the introduction of the Drift into the district.

The erratics are believed to have been assembled under glacial conditions, evidently over a long interval of time, early in the Pleistocene Period. The Drift is older than the 140-foot and 100-foot terraces of the Upper Thames Basin; the former contains early Chellean implements and the latter a Chellean fauna. It is believed to be younger than the Cromer Forest Bed, containing earliest Palæolithic implements and a late Pliocene fauna. It seems to be older than the 'Preglacial' beach of the Bristol

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[1] The Rev. C. Overy, Abstracts Proc. Geol. Soc. No. 1095 (1923) p. 28.

Channel, since a Chellean fauna comparable with that of the 100-foot terrace of the Thames is found in caves associated with the beach, the Preglacial age of which is viewed with some suspicion on this and other evidence.

Within the district a threefold glacial sequence is now established. It is emphasized that the first, the subject of this paper, was the maximum glaciation of the Southern Midlands and of early Pleistocene age. During the other two the district was an ice-free land-area, between the glaciers of the Eastern Counties and of Wales, and it is suggested that the rocks from distant places, including the older centres of glaciation, no longer enjoyed the freedom of dispersal of the early episode. The Oxford district being ice-free during these later glacial episodes, the conditions which then prevailed are faithfully recorded in the contemporary fluviatile deposits and surface-changes. In East Anglia and elsewhere the remains of the early glaciation have been destroyed, or nearly so; they may be incorporated in the younger Boulder Clays.

The chronological sequence, based on this and two earlier papers, is as follows[1]:—

I.	Plateau Drift with erratic material, maximum of glacial conditions within the district.	Mindel.
	Chellean implements and 'warm fauna.' 140- and 100-foot terraces.	M R.
II.	40 to 50-foot terrace (Wolvercote)? and older Gravels of the 20-foot terrace (Summertown) with 'cold fauna' and older Acheulean implements.	Riss.
	Period of aggradation: Younger Gravels of the Summertown Terrace, with marked 'warm fauna' and Upper Acheulean implements, followed by Gravels and Sands of the Wolvercote Channel with 'warm fauna', Upper Acheulean and Micoque implements.	R W.
III.	Silts and Clays, with Reindeer and Mousterian (?) implements, filling the Wolvercote Channel: disturbed by 'Warp Sands' and Trail, which descended over older terrace-gravels as the river re-excavated its bed and dug its buried channel.	Würm.

December 19th, 1928.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

Dr. C. A. MATLEY gave a short account, illustrated by lantern-slides, of a visit to the crater of Papandajan (Java) on January 7th, 1925, at which date, and for some twelve months previously, it was under observation by Dr. N. J. M. Taverne, of the Dutch East Indies Mining Service. The crater was closed to the public owing to a recent fatality, and Dr. Matley expressed his indebtedness to the Director for special permission to visit it, and also to Dr. Taverne for acting as guide and for explaining his methods of vulcanological research.

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[1] Q. J. G. S. vol. lxxx (1924) pp. 113 *et seqq.* & *ibid.* vol. lxxxi (1925) pp. 62 *et seqq.*

The crater and its wall had been mapped on the scale of 1 : 2000, with contours, and all the vents and fissures recorded. The temperatures of the fumaroles, solfataras, hot springs, and mud-holes were taken daily. A seismometer and a Milne seismograph had been installed, and another of improved type was about to be erected. A torsion-balance had been ordered, with the object of ascertaining changes of mass in the volcano and detecting movements of the magma. The problem of determining the stages leading to an eruption and, if possible, of predicting it, was therefore being attacked from three sides: namely, temperature, crustal movement, and movement of magma. In addition, the nature and quantity of the gaseous emanations, and the changes in them, were also being studied. The general conclusion drawn at the time of the visit was that the mass of lava was rising, but had not yet come directly into action, as the volcanic ash thrown out at recent eruptions consists of previously consolidated and propylitized material, and no new lava is present in it. The study of this volcano is of importance, as no fewer than 3000 lives were lost in the eruption of 1772.

Descriptions were given of the phenomena seen, including the destruction of part of a forest by a recent eruption of propylitized ash. A full account of the observations by Dr. Taverne will be found in 'Vulkanologische Berichte' vol. xxxiii. (1924) & vol. xlii. (1925), as also in 'Vulkaanstudien op Java' 1926.

January 9th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

Prof. Owen Thomas Jones, M.A., D.Sc., F.R.S., F.G.S., delivered the following lecture (illustrated by lantern-slides) on the History of the Yellowstone Cañon (Yellowstone National Park) U.S.A.:—

The Yellowstone Cañon is one of the most striking features of the Yellowstone National Park, which has long been famous for its geysers and its Tertiary volcanic rocks.

The Park has an area of 3344 square miles, which is almost equal to the combined area of Lancashire and Cumberland.

After leaving Yellowstone Lake, the Yellowstone River flows northwards through the Hayden Valley with a very small gradient. Both around the lake and in the Hayden Valley there are remains of several post-Glacial lake-terraces. The river then drops over the Upper Fall (108 feet), and in a short distance over the Lower Fall (309 feet). The so-called 'Grand Cañon' begins here, and extends to Tower Falls about 20 miles away to the north, where the very narrow precipitous 'second Cañon' begins. At the lower end of this cañon the Yellowstone is joined by the Lamar River, which flows in a wide-open, flat-floored valley, of great size and mature aspect. Below the junction of the rivers the so-called 'third Cañon' commences, and continues downstream towards Gardiner.

A preliminary geological survey of the Park was made by Dr. F. V. Hayden, who had among his assistants the famous delineator of geological subjects, W. H. Holmes, who, besides being a skilled artist, possessed unusual ability as a geological observer. The account of the geology of the Park in Hayden's Final Report for the year 1878 was contributed by Holmes, and this is still the best account of the physical features of the Park. In later years the Park was surveyed in detail by a field unit of the U.S. Geological Survey, under Arnold Hague, and a folio of maps, together with a summary description of the geology, was published in 1896.

The igneous rocks were described by Iddings in Monograph 32, Part II. Reference is made in this Monograph to the account of the physiography of the Park by Hague in Monograph 32, Part I. It appears, however, that the manuscript of this Monograph was not completed when Hague died, and it was never published.

The lecturer was privileged last summer to be the guest of the Summer School of Geology & Natural Resources, which was organized and conducted by Prof. R. M. Field, of Princeton University. During the visit of the Summer School two years previously, Prof. Field had photographed with a cinematograph camera a part of the cañon below the Great Fall, and, when the film was exhibited, he observed cross-bedded sediments on the side of the cañon near the prominent pinnacle known as Red Rock. Last summer Prof. Field and the lecturer examined these sediments in the company of Mr. W. J. Johnson, of the Canadian Geological Survey, and Prof. W. A. Parks, of Toronto University, and they found about 187 feet of alternating blue silts, yellow sands, and conglomerates, with a calcareous and tufaceous cement. The silts could only have been deposited in quiet water, and resemble lacustrine deposits. Similar sediments were observed on this occasion within 50 feet of the bottom of the cañon and about 100 yards of the foot of the Great Fall, and also in the ravine between the two falls where they are capped by a conglomerate at a level of about 100 feet above the Upper Fall. These sediments show that, since the cañon was eroded, it has been dammed somewhere below this locality, and filled to the brim with sediments. It is the prevalent opinion among physiographers that the cañon is of post-Glacial date, and the conglomerate capping the sedimentary series between the falls has been interpreted (E. de Martonne) as one of the Yellowstone Lake terraces. The conglomerate is, however, pre-Glacial, and appears to have nothing to do with the lake-terraces. A study of the geological maps in the folio suggests that the cañon was dammed by great flows of lava, which moved up it from the direction of Gardiner, and reached both the 'Grand Cañon' and for many miles up the Lamar Valley. Some of these flows consist of trachytic rhyolite, but most of them consist of basalts which are now preserved as remnants on the flanks of the cañon, descending in places to within about 100 feet of its floor and rising in places to a height of nearly 8000 feet. As the top of the sedimentary series between the two falls stands at about 7800 feet, it is obvious that the lava-flows would be capable of damming the cañon to the depth necessary to allow of the formation of the sediments. The evidence of the sections exposed in the walls of the 'Second Cañon' near Tower Falls clearly shows that, in that region, an older cañon lying to the east of the 'Second Cañon' had been filled by alternations of basalts and conglomerate, and the present 'Second Cañon' has been excavated to one side of the old blocked cañon.

A consideration of the profiles of the Yellowstone Cañon, the Lamar River, and their tributaries shows that traces of three cycles of erosion are preserved. In the Yellowstone system the first cycle is represented by the Hayden Valley, the second cycle by the 'Grand Cañon,' and the third cycle by the 'second' and 'third' cañons. The lava-flows were poured out on the floor of the valley while the third cycle of erosion was in progress. The 'Grand Cañon,' which belongs to the earlier or second cycle, has been eroded through the rhyolitic rocks of the Park. The basalts which followed on the third cycle are, therefore, obviously younger than the rhyolites. The conglomerate between two of the basalt-flows has yielded the remains of a Pliocene horse, and is presumably of Upper Pliocene age.

The lecturer considered that a very great interval of time intervened between the eruption of the rhyolites and the eruption of the basalts. In the folio, however, the rhyolites are regarded as being younger than the basalts and conglomerate, an interpretation which is quite inconsistent with the physiographical history of the cañon, and also with the direct evidence in the field. A perusal of Holmes's report shows that he had grasped nearly all the significant points in the geological history of the region, and there is no doubt that, given a little more time, he would have completely anticipated the results obtained by Prof. Field and the lecturer.

The general volcanic history of the Park appears, then, to have been as follows. A vast thickness of andesitic breccias was poured out, either in late Cretaceous or in early Eocene times, on a very uneven surface which consisted of rocks ranging from Pre-Cambrian to Cretaceous. A long period of erosion intervened, and the surface of the andesitic breccias was dissected into a system of mature or sub-mature valleys. On to this surface the rhyolites were poured out. There is reason to believe that the surface of the rhyolites themselves had been peneplaned, and several hundreds of feet of the upper part of the rhyolites had been removed, before the initiation of the 'Grand Cañon' cycle, which was presumably the result of uplift. A further rejuvenation initiated the third cycle of erosion, represented mainly by the 'third' cañon, after which the basalts and trachytic rhyolites were erupted, leading to the damming of the 'Grand Cañon' and the deposition of the sediments near the falls. Since that presumed Upper Pliocene period, the basalts have been almost completely removed to a depth in places of nearly 1500 feet, the sediments in the 'Grand Cañon' have been almost cleared out, and the erosion of the cañon, which had been arrested for an enormous period of time, has been resumed.

Two facts are very significant in connexion with the history of the region. One is the very large amount of material that has been removed from the whole length of the cañon since Upper Pliocene times, and the other is that the Great Fall of the Yellowstone has probably remained in its present position for an enormous period of time, and may perhaps be regarded as the oldest fall in the world.

January 23rd, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communications were read:—

1. 'The South Wales End-Moraine.' By Prof. John Kaye Charlesworth, D.Sc., Ph.D., M.R.I.A., F.G.S.

The Irish-Sea Ice stood over Cardigan Bay at the period of the maximum advance of the Newer Drift period, and ponded back the natural drainage of Northern Pembrokeshire and Southern Cardiganshire to form a chain of extra-glacial lakes connected by marginal streams. This drainage, except at an early stage, failed to escape across the main watershed into the Bristol Channel, and was led along the ice-edge into Cardigan Bay. The largest lake occupied the valley of the Teifi, and was 34 miles long.

The end-moraine of the Newer Drift passes across Eastern and Southern Wales. In Northern Pembrokeshire and Southern Cardiganshire, where the moraine is rarely conspicuous and often absent over considerable stretches, it was laid down along the edge of the Irish-Sea Ice, contemporaneously with the operation of the highest marginal channels of these areas.

Farther east, the moraine is practically continuous, and represents the marginal product of the local Welsh Ice, which was centred in the mountains of Central Wales, the Carmarthenshire Vans, the Brecon Beacons, the Black Mountains, and the mountains of Radnor Forest. This ice flowed beyond the outlets of the great valleys of the east to form the valley-glaciers of the Severn, Clun, Lugg, Arrow, Wye, and Usk, and extended southwards on to the coastal plain of Glamorgan as the Glamorgan Piedmont Glacier and the Swansea Bay Piedmont Glacier. The end-moraine is disposed in loops around these glaciers, and passes beneath or near the following places: Tregaron, Swansea, Kyle, Cowbridge, Cardiff, Risca, Usk, Abergavenny, Pandy, Hereford, Wellington, Leominster, Craven Arms, and Montgomery.

This Newer Drift, which probably marks the culmination of the cold of the Glacial Period in Britain, is shown to be of early Magdalenian age by the collective evidence of the Upper Palæolithic implements of Britain. It was preceded by the 'Aurignacean

Oscillation', the minimum extent of which can be estimated from the distribution of the remains of the Pleistocene mammalia in the drifts and caves of the North of England.

The raised beach of the southern part of the British Isles is earlier than the Older Drift.

2. 'The Glacial Geology of the Derbyshire Dome and the Western Slopes of the Southern Pennines.' By Albert Jowett, D.Sc., F.G.S., and Prof. John Kaye Charlesworth, D.Sc., Ph.D., M.R.I.A., F.G.S.

The Derbyshire Dome of the Southern Pennines was overridden at the period of maximum glaciation by ice from the north and north-west. This is shown by the occurrence of fairly extensive patches of true Boulder Clay, ranging up to 20 feet in thickness, by the wide distribution of erratics of Lake District and Galloway rocks over the dome and along its valleys, and by a southward carry of the local rocks, such as Carboniferous Limestone (dolomitic and non-dolomitic, cherty and non-cherty varieties), Millstone Grit, and Toadstone.

The upper limit of the Galloway and Lake District erratics follows the outer flanks of the South-Western Pennines at an average height of about 1250 feet above sea-level, decreasing slightly southwards in the direction of flow.

The ice-recession from this position was associated with a copious marginal drainage, which eroded a well-developed suite of channels linking a number of big extra-glacial lakes in the valleys of the Western Pennines. These waters escaped at the same successive stages: (1) by the Walsden Gorge into the Todmorden valley and the Humber drainage; (2) by Dove Holes into the Wye, Derwent, and Trent basins; (3) into the Trent drainage by its tributaries north and west of Stoke-upon-Trent and by the Rudyard Gorge, north of Leek; and (4) by the Market Drayton Gap into the Severn and the Bristol Channel.

February 15th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President in the Chair.

In his Anniversary Address, dealing with the Geological History of the Atlantic Ocean, the President remarked that the Atlantic is the best test case for the theory of the permanence of the ocean basins. According to one view, the Atlantic trough is a primæval geographic feature and dates back to the pre-Palæozoic. According to an alternative view, it has been repeatedly so broken up by lands trending east to west across it that there was no sea entitled to the name of the Atlantic.

The Icelandic Ridge, the northernmost of these cross lands, is generally accepted, and it was probably finally severed between the Upper Palæolithic and the Neolithic. This land is shown by

varied evidence from different geological periods to have extended as far south as a line from Newfoundland to Ireland, or to the Azores. It formed the northern shore of the Tethys. The main issue regarding the Atlantic relates to the southern side of the Tethys and the Brazilio-Ethiopian land. That the South Atlantic was occupied by land in the Palæozoic Era is indicated by the absence of marine rocks from most of both coasts. From Upper Carboniferous to Lower Jurassic times Brazil and Africa were parts of Gondwanaland, and a southern fauna and flora ranged through both. The invasion of this land by the sea began in the Middle Cretaceous Period, with gulfs from the Mediterranean which reached Brazil and Angola: they were closed to the south, as the marine fauna of Cape Colony is distinct, and ranged westwards through Chile, and as the freshwater fauna was continuous between Africa and South America. This continuity is shown by the river fishes, porcupines, lizards, snakes, and many invertebrates, of groups that were in existence in the Lower Kainozoic Era. The evidence shows that the connexion lasted till the end of the Oligocene; but it cannot have lasted much later, as the more specialized mammals and birds, for instance, the humming-birds, did not use it as a land bridge. The existence of this land-connexion in Oligocene times is shown by the occurrence of the same shallow-water marine animals in the West Indies and in the Mediterranean. Some of them might have crossed by a chain of islands, but that the land was continuous is shown by the marine mollusca of the West Indies and the Mediterranean being distinct from those in the south. The first commingling in South America was in the Upper Miocene (Entrerios Beds) according to H. von Ihering. A slight temporary land-connexion was established in the Upper Miocene, as shown by the migration of *Hipparion gracile* to Europe and of African antelopes to the United States.

This land-connexion was severed too early to have served as Atlantis, though the Canaries may have been joined to the mainland up to the Pleistocene. There is no geological evidence of any land-connexion of Africa and South America in the time of Man.

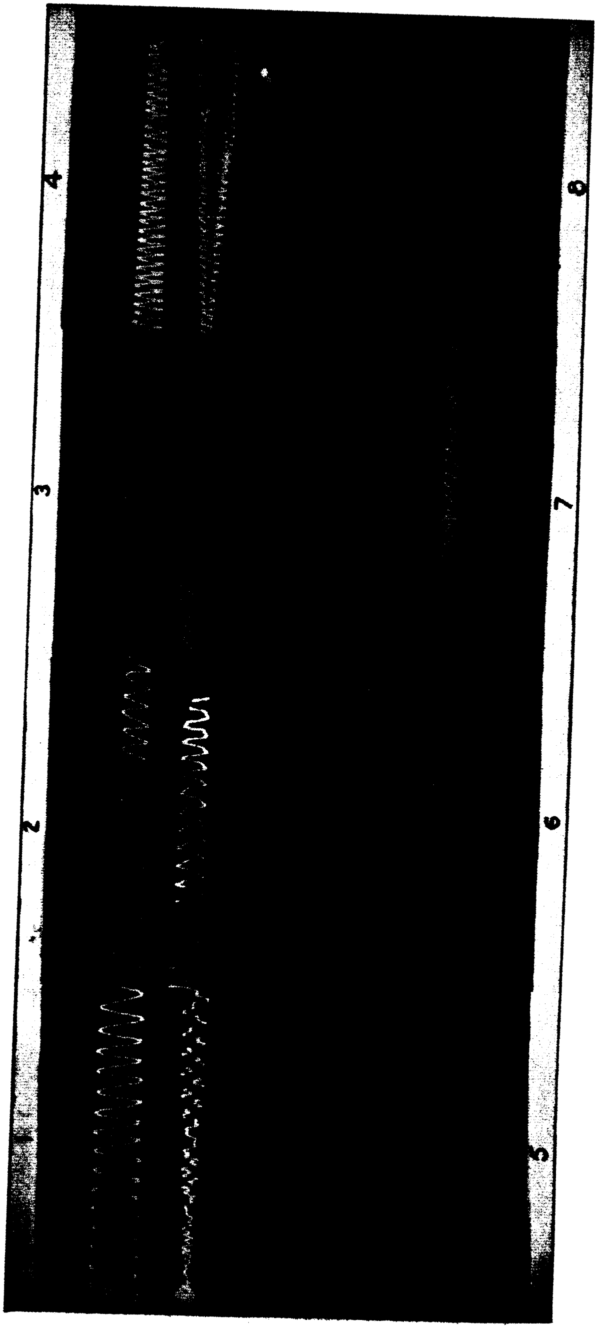
The Atlantic is a relatively young geographical feature and due, as held by Suess, to the growth of two gulfs, which projected northwards and southwards from the Tethys. These gulfs were formed by subsidences which began in the Middle Cretaceous and have continued to the Pleistocene, and they finally united the Arctic, the North Atlantic (Poseidon), and the Nereus of the South Atlantic. The Atlantic trough is the greatest of meridional geographical features, and is due to the collapse of a belt of the crust along faults and tensional fractures connected with the pressure of South America westward against the Andes.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

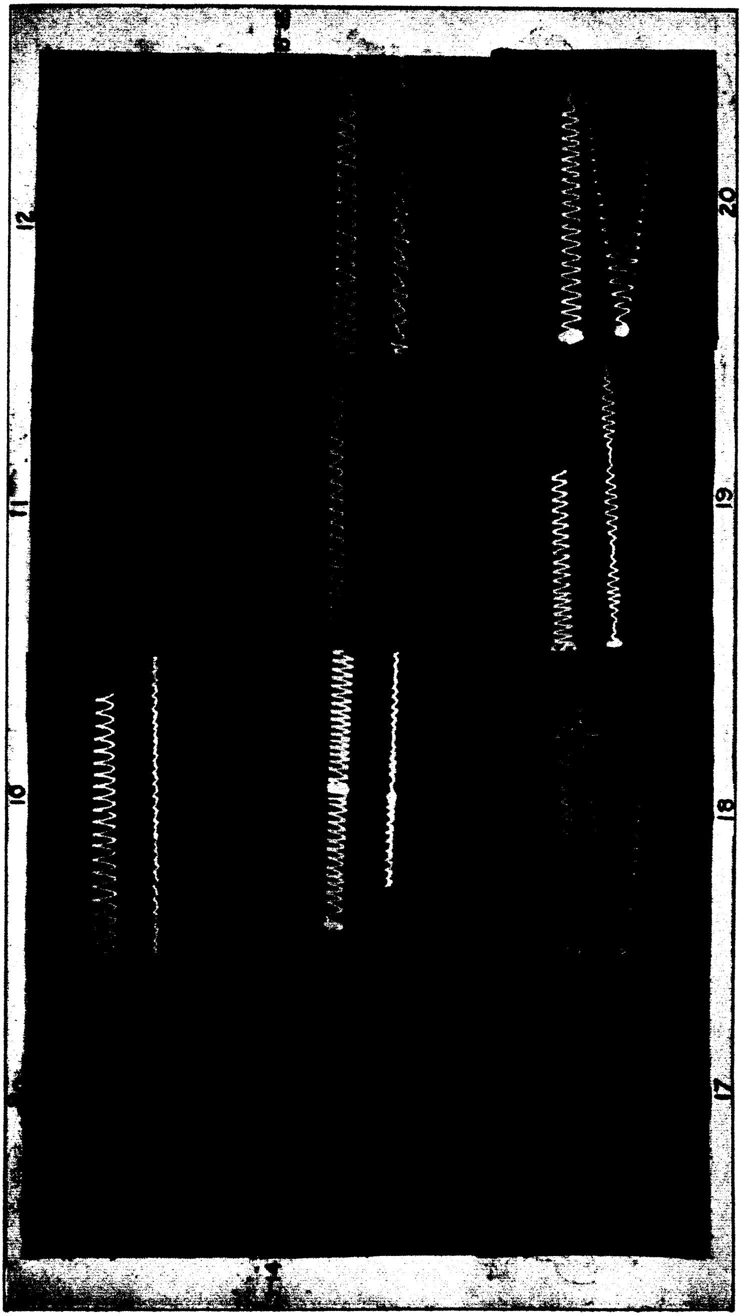
BROWNING.

Phil. Mag. Ser. 7, Vol. 7, Pl. XVI.

FIGS. 1-8.



Figs. 9–20.



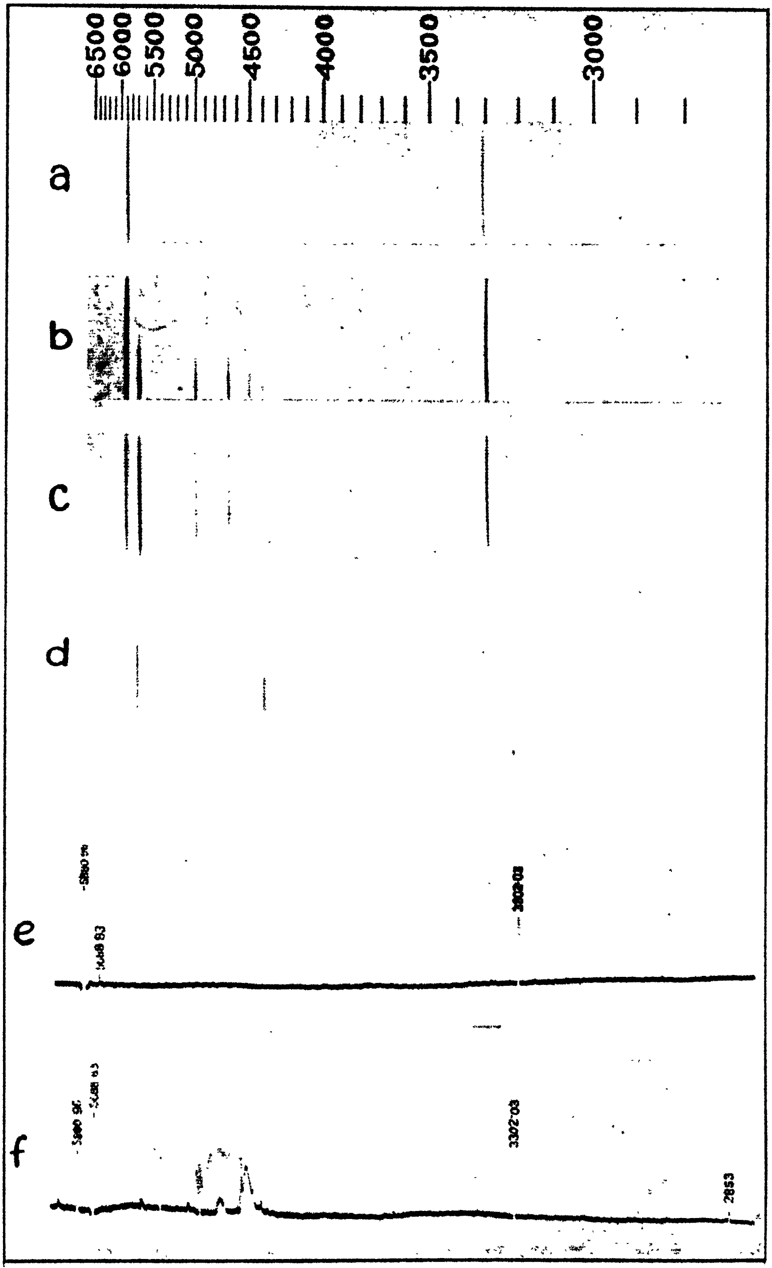

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Fig. 1.

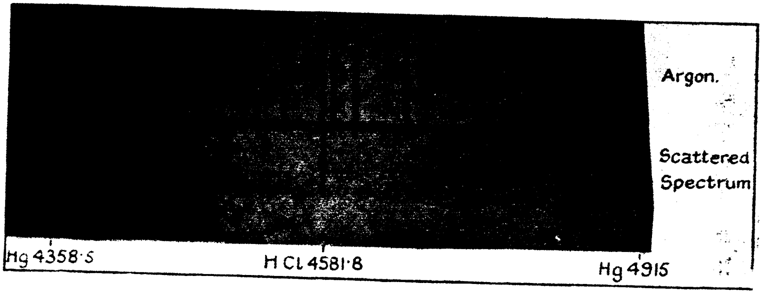
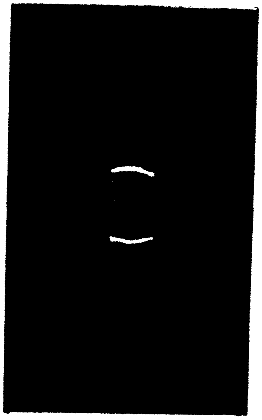


Fig. 2.

Fig. 3.



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AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

MAY 1929.

XCII. *The Crystal Structure of Solid Methane.* *By* J. C. McLennan, *D.Sc.*, *F.R.S.*, *and* W. G. Plummer, *Ph.D.*

THE structure of the methane molecule has recently become a most interesting subject of discussion among theoretical physicists and chemists. According to some authorities, the results of recent work in the field of Atomic Physics are said to demand a pyramidal structure for the molecule instead of the hitherto universally accepted tetrahedral structure. In much of the literature upon the subject the state of the molecule under consideration is left entirely unspecified.

The present paper deals with an X-ray investigation by the "powder" method of analysis of solid methane at temperatures intermediate between those of liquid air (−190° C.) and liquid hydrogen (−255° C.). It is to be understood, in speaking of *the* molecule, that the *crystal* molecule is implied throughout, and the question of the relationship which it may bear to the chemical molecule will not be discussed here.

Any attempt at a complete determination of structure by the "powder" method alone must necessarily be open to a considerable amount of criticism, but at the present time the growth of single crystals of methane and their maintenance over a period sufficiently long for X-ray examination is not practicable; for this purpose a constant supply of liquid

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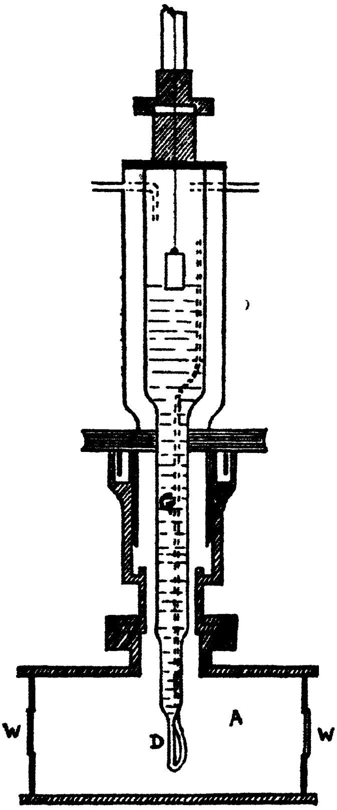
[*] Communicated by the Authors.

hydrogen would be required. Hence, although it may not be permissible to regard the suggested structure as more than an approximation to the true one, the results of this examination definitely prove the existence of a cubic modification for solid methane over the temperature range of these experiments.

Fig. 1.



Apparatus.

A Debye-Scherrer type of camera, which closely resembled that described in a previous paper (1), was employed (fig. 1). After loading the cylindrical film-holder and placing it in the correct position in the camera (already determined by preliminary experiment), the edges of the loose lid were covered with a small quantity of a preparation of petrolatum and beeswax, and the lid was firmly held in position by means of six clamps. The main chamber A was then evacuated for several hours by means of suitable pumps, a liquid-air trap having been inserted next to the chamber to prevent any mercury-vapour from reaching it. Next, the nickel-silver container G was filled with liquid hydrogen, and an interval of a quarter of an hour allowed for the cooling of the apparatus, after which a small quantity of pure methane was admitted to the main chamber from a side tube (the tap connecting the main chamber with the pumps having, of course, been closed just previously to introducing the methane). The deposition of crystals of solid methane on the outside of the copper capillary tube D could be observed through the window W, and when a layer of the desired thickness had formed, the crystalline powder was irradiated with X-radiation generated by a Shearer tube and suitably filtered to exclude β-lines. The rays passed into the camera through a lead slit 1 mm. wide which formed part of the camera, and was covered on the outside with thin aluminium foil. The exposure varied from 5 to 10 hours, with a current of approximately 6 milliamperes through the tube. Owing to the gradual decrease in thickness of the methane layer during the exposure, it was found advantageous to observe the layer carefully during the first stages, and to admit fresh methane when required. (Incidentally this procedure assisted in producing a more random orientation of crystals than would otherwise have been the case.)

Preparation of Methane.

Owing to the comparative ease with which most substances crystallize at liquid hydrogen temperatures, it is of the utmost importance that the methane employed shall be of the highest possible purity. Every precaution was taken to exclude impurities, and separate X-ray photographs under the same experimental conditions were taken of solid methane prepared by two different methods; the diffraction patterns obtained were apparently identical in the two cases.

In the first method methane was prepared by dropping a mixture of equal parts of methyl iodide and 95 per cent. methyl alcohol from a stoppered bottle into a large quantity of freshly-prepared zinc-copper couple. The gas, after being passed over another zinc-copper couple, was collected over distilled water and afterwards passed through tubes containing phosphorus pentoxide. Spectroscopic examination showed the gas to be free from nitrogen and possible iodide impurity, and the only bands in evidence were those associated with the elements carbon and hydrogen.

The second method of preparation was from aluminium carbide and water. The flask, delivery tube, etc., were evacuated before commencing the reaction in order to save the trouble of displacing air in the apparatus. The gas was collected over distilled water and purified by bubbling it slowly through a solution of potassium dichromate and concentrated sulphuric acid. It was then passed through a caustic potash tube and two tubes containing phosphorus pentoxide. The final product was subjected to spectroscopic examination, and no bands other than those characteristic of carbon and hydrogen and CH compounds were observed.

After each exposure the communicating tap between the pumps and the main chamber was closed, and the frozen methane upon the capillary tube was allowed to warm up slowly until it reached the gaseous state. Samples of this methane were then examined spectroscopically for impurities, and the absence of nitrogen and oxygen bands indicated that air had not leaked into the chamber during the course of the experiment. This point was capable of further verification on development of the X-ray film, upon which no "powder" lines for those elements were observed.

Crystallographic Information.

The melting and boiling points of methane are given in the International Critical Tables(2) as −184° C. and −161°·4 C., respectively. In 1912 W. Wahl(3) found that pure methane crystallized very readily when cooled with liquid air under exhaust, and that the growth structures were always developed according to the hexahedron, and closely resembled those of ammonium chloride. The more rapid the crystallization, the finer were the resulting growth structures. The crystals were found to be isotropic; the molecule must therefore possess the four trigonal axes of symmetry characteristic of the cubic system, and consequently the valency directions must be assumed to make equal angles with one another. This argument applies also to the cubic forms of carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, and tetramethylmethane.

Each of these compounds shows a low-temperature doubly-refracting modification; similarly for methane at very low (liquid hydrogen) temperatures Wahl(4) observed an enantiotropic transition into a doubly-refracting form.

Experimental Results.

For seven of the eight "powder" photographs obtained for solid methane the freezing agent employed was liquid hydrogen; in the case of the remaining one liquid air under reduced pressure was used. Apart from slight displacements of the lines attributable to differences in thickness of the various layers, the X-ray patterns were apparently the same in all cases, and were typical of the cubic modification. Variation of the experimental conditions so as to favour the formation of the doubly-refracting modification observed by Wahl produced no change in the photographs. This is rather surprising, but the probable explanation is that, owing to inefficient heat insulation, a not inconsiderable temperature gradient existed between the inside of the copper capillary tube in contact with the liquid hydrogen and the exterior layers of crystals frozen upon the outside of this tube which were being photographed.

Four of the exposures were made with characteristic zinc K radiation and the remaining four with iron K_α-rays. The photographs obtained with the latter radiation were not so clear as those made with the zinc rays on account of the higher dispersion, and consequently broader lines, but the experimental spacings are in close agreement in the two cases. (Compare Tables I. and II. with Tables III. and IV.)

Table I. shows the derivation of the experimental spacings from measurements of the lines upon a typical "powder" photograph of solid methane (prepared in this case from methyl iodide and irradiated with zinc rays). As a very thick layer of methane was employed, the lines due to the copper of the capillary tube were scarcely visible, and have been excluded from the table. The approximate intensities of reflexion are indicated by the customary symbols: V.S., M., etc. The theoretical spacings in column 4, which correspond to the planes opposite them in column 5, have been calculated upon the assumption of a unit cube of edge 6·35 Å.

In order that more precise values of the longest spacings which occur might be obtained, together with a more accurate representation of the relative intensities of reflexion from the various planes, a very thin layer of solid methane was exposed (also to zinc radiation), for a shorter period; the resulting spacings are given in Table II. In consequence of the reduced exposure, only four lines (in addition

TABLE I.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}434$ Å. Copper filter.
Copper capillary tube. Exposure : 8½ hr.
Correction for the thickness of the layer = − 0·12 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
5·165 W. to M.	42° 03½′	1·070	1·075	135
4·805 W.	39 06½	1·137	1·123	440
4·44 M.	36 09	1·215	1·222	115 and 333
4·155 M.	33 48½	1·289	1·296	224
3·70 M.	30 08½	1·428	1·420	240
3·595 V.W.	29 15	1·468	1·456	133
3·30 V.W. to W.	26 51½	1·587	1·588	400
......	......	......	1·835*	222
2·715 V.S.	22 06	1·905	1·914	113
2·295 V.S.	18 38	2·244	2·246	220
1·65 M.	13 26	3·09	3·18	200
1·395 V.S.	11 21½	3·64	3·67	111

* The presence of a reflexion from this plane cannot be established owing to a line from the copper capillary tube at a point corresponding to 1·801 Å.

TABLE II.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}434$ Å. Copper filter.
Copper capillary tube. Exposure : 7¼ hr.
Correction for the thickness of the layer = − 0·07 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
2·705 M. to S.	22° 01′	1·913	1·914	113
2·30 V.S.	18 43	2·235	2·246	220
1·62 M.	13 11	3·144	3·176	200
1·39 V.S.	11 19	3·655	3·667	111

to those given by the copper tube, which have been omitted from the table), were sufficiently intense to be measurable ; in this case the methane was prepared from aluminium carbide.

The spacings resulting from the measurement of two other films are derived in Tables III. and IV.; the remaining photographs have also been measured, and give, within the limits of experimental error, similar values.

Table III.—Methane Frozen with Liquid Air under Reduced Pressure.

Iron X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}934$ Å.
Copper capillary tube. Exposure: 6 hr.
Correction for the thickness of the layer = − 0·16 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
4·64 W. to M.	37° 45½′	1·58	1·588	400
3·71 W. to M.	30 12	1·92	1·914	113
3·12 W. to M.	25 24	2·25	2·246	220
2·25 W.	18 19	3·08	3·176	200
1·88 M.	15 18	3·66	3·667	111

Table IV.—Methane Frozen with Liquid Hydrogen.

Iron X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}934$ Å. Manganese filter.
Copper capillary tube. Exposure: 5½ hr.
Correction for the thickness of the layer = − 0·09 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
3·74 M.	30° 27′	1·91	1·914	113
3·11 M.	25 19	2·26	2·246	220
2·24 M.	18 13½	3·09*	3·176	200
1·89 M. to S.	15 23	3·65	3·667	111

* This line was particularly broad, and difficult to measure accurately.

Returning to Table I., the experimental spacings in column 3 are seen to be in very close agreement with those calculated for a face-centred cubic cell of edge 6·35 Å., which are given in column 4. Within the range of spacings shown, the only irregularity is the indefiniteness as to whether there is a reflexion from the (222) plane corresponding to 1·835 Å.; if such a reflexion exists, it is indistinguishable in the photographs from a line corresponding to 1·801 Å., for which the copper capillary tube is responsible. (It was intended to settle this point by making an exposure with a capillary tube of some suitable metal other than copper.) Further, all planes which do not satisfy the condition for a face-centred lattice are absent. The density of liquid methane at approximately its boiling-point has been given as 0·415 gm./c.c.(5), and if this be used as an approximation to the density of the solid, then :

$$\text{No. of molecules per unit cell} = n = \frac{0{\cdot}415(6{\cdot}35)^3}{16{\cdot}03\,.\,1{\cdot}649} = 4{\cdot}02\,;$$

that is, there are four molecules per unit cell. There are no abnormal spacings except those demanded by a face-centred lattice, hence all the following space-groups have to be considered :

$$T^2,\ T_h^3,\ T_d^2,\ O^3,\ O_h^5.$$

If the further assumption is made that all the carbon atoms are crystallographically identical, and that all the hydrogen atoms are identical in this sense, only two of these, T^2 and T_d^2 give four equivalent positions for the carbon atoms and sixteen equivalent positions for the hydrogens(6). In either case the four carbons in the positions of fourfold symmetry without any degrees of freedom will have coordinates :

$$000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0\,;$$

the carbons themselves having symmetry T in the case of the space-group T^2, and T_d for the space-group T_d^2. The sixteen hydrogens in positions of 16-fold symmetry with one degree of freedom u will have coordinates :

$$\begin{array}{llllllllllll}
u, & u, & u; & u, & \bar{u}, & \bar{u}; & \bar{u}, & u, & \bar{u}; & \bar{u}, & \bar{u}, & u; \\
u, & u+\frac{1}{2}, & u+\frac{1}{2}; & u. & \frac{1}{2}-u, & \frac{1}{2}-u; & \bar{u}, & u+\frac{1}{2}, & \frac{1}{2}-u; & \bar{u}, & \frac{1}{2}-u, & u+\frac{1}{2}; \\
u+\frac{1}{2}, & u, & u+\frac{1}{2}; & u+\frac{1}{2}, & \bar{u}, & \frac{1}{2}-u; & \frac{1}{2}-u, & u, & \frac{1}{2}-u; & \frac{1}{2}-u, & \bar{u}, & u+\frac{1}{2}; \\
u+\frac{1}{2}, & u+\frac{1}{2}, & u; & u+\frac{1}{2}, & \frac{1}{2}-u, & \bar{u}; & \frac{1}{2}-u, & u+\frac{1}{2}, & \bar{u}; & \frac{1}{2}-u, & \frac{1}{2}-u, & u.
\end{array}$$

If the space-group T^2 is under consideration, the symmetry of the hydrogen atom itself will be C_3; but if the correct space-group is T_d^2 this symmetry will be C_{3v}.

The next step is to calculate the resulting theoretical intensities for the various values of the parameter u, and to ascertain which particular value of u gives the best agreement with the observed intensities. This work has been summarized in Table V., which shows the intensities of the various planes relative to the standard value 15 arbitrarily chosen for the (111) plane. The formula employed was

$$\text{Intensity} \propto Q\,.\,Z\,.\,S^2,$$

where S is the structure factor, which depends upon the

TABLE V.

Intensities Calculated for Various Values of the Parameter u.

Plane.	Q factor.	Z.	Intensity relative to that of the (111) plane, taken as 15.							Experimental intensity.
			$u=0$.	$u=0{\cdot}1$.	$u=0{\cdot}13$.	$u=0{\cdot}15$.	$u=0{\cdot}18$.	$u=0{\cdot}2$.	$u=0{\cdot}22$.	
440	2¼	12	2·1	2·3	3·9	3·1	1·6	1·7	0·3	W.
115 & 333	2½	24 & 8	6·3	1·8	3·1	4·2	4·8	4·3	4·5	M.
224	2½	24	4·7	2·6	3·2	3·4	3·7	4·6	6·7	M.
240	3	12 or 24	2·8 or 5·7	1·5 or 3·0	2·0 or 4·1	2·7 or 5·3	2·9 or 5·9	1·4 or 2·8	0·6 or 1·2	M.
133	3	24	5·7	3·6	6·0	7·6	7·3	5·4	5·2	V.W.
400	3½	6	1·7	0·2	0·1	0·2	1·0	1·8	0·2	V.W. to W.
222	5	8	3·2	2·1	2·7	2·9	1·8	1 0	0·6	—
113	5¾	24	11	4·5	4·4	4·6	6·3	8·2	9·6	V.S.
220	8½	12	8·1	4·8	5·2	6·3	9·6	12	1·2	V.S.
200	17½	6	8·3	6·2	5·0	3·5	2·1	1·3	0·8	M.
111	23¾	8	15	15	15	15	15	15	15	V.S.

geometrical positions of the atoms and on their scattering-powers. As a first approximation, the latter were taken as proportional to the atomic numbers (C=6, H=1). The Q factor referred to in column 2 was calculated from

$$Q=\frac{1+\cos^2 2\theta}{2}\cdot\frac{1}{\sin^2\theta\,.\,\cos\theta},$$

where θ is the glancing-angle.

The "Z" number represents the number of cooperating planes, and it will be noted that, in the case of the (240) plane, its value may be 12 or 24, according to whether the space-group is T_2 or T_d^2 respectively; hence, until the question of the correct space-group is settled, there will be for this plane two possible values for the resulting intensities. The temperature factor was not introduced into the intensity formula, as its effect should be almost negligible at the temperatures used in these experiments.

The particular case of $u=0$ is equivalent to disregarding entirely the scattering effect of the hydrogen atoms; or, alternatively, to considering that the four valency electrons from the four hydrogen atoms in the CH_4 molecule have joined the four outer electrons belonging to the carbon atom, thus forming a scattering system of eight electrons per molecule, which should be a stable configuration. It is extremely probable that such systems would be very nearly identical for each molecule throughout the structure; hence each system might be regarded, for the purpose of scattering, as the true structural unit, and might conveniently be supposed to be concentrated at the centre of the carbon nucleus (since it is the same for each molecule). If this be the case, the X-ray results will give no indication of the distance from the centre of the carbon nucleus to the orbit in which the electrons rotate; it will only be possible to determine the distance from one molecule to the next. A comparison of the experimental and theoretical intensities for the various values of the parameter u in Table V. shows that no value of u gives very good agreement, but $u=0$ apparently gives the nearest correspondence, though the observed reflexion from the (133) plane is too weak. A more encouraging agreement is obtained if, in the calculation of the theoretical intensities, the scattering effect of the hydrogen atoms be neglected ($u=0$), and the factor f given by Ponte(7) for reflecting power of the carbon atom for high-frequency rays (which varies with the spacing) be used instead of the constant factor 6 for the carbon atom. The values of f given in Table VI. are taken from Curve III. of Ponte's paper, and the square of this factor has been used in the calculation of the theoretical intensities given in column 3 of the table; the Lorentz factor, the geometrical structure factor, and the factor for the number of cooperating planes have also been taken into consideration in this calculation. With the exception of the reflexions from the (111), (200), and (133) planes, which are not sufficiently strong, the observed intensities (taken from Table I.) agree quite well with the corresponding theoretical values. It is only fair to add that the lines corresponding to the (111) and (220) planes in the photographs obtained with zinc radiation (Tables I. and II.) are so strong that no further blackening of the film would be detectable, and the next stage would be reversal; this might explain why the (111) reflexion is not stronger in the photographs than that from the (220) plane. However, the comparative weakness of the (200) reflexion still remains unexplained, but in all the photographs the line corresponding to this plane is noticeably broader than the remainder, and this fact cannot very well be taken into account in ordinary eye-estimations of the relative intensities of the lines.

TABLE VI.

Calculated Intensities using the Ponte Factor.

Plane.	*f*.	Theoretical intensity proportional to :	Observed intensity (from Table I.).
440	1.5	1·0	W.
115 & 333	1·6	3·4	M.
224	1·73	3·0	M.
240	1·90	2·1 or 4·3	M.
133	1·95	4·5	V.W.
400	2·15	1·6	V.W. to W.
222	2·45	4·0	—
113	2·6	15	V.S.
220	3·0	15	V.S.
200	4·05	28	M.
111	4·5	63	V.S.

V.S.=Very strong; S.=Strong; M.=Moderately strong; W.=Weak; V.W. to W.=Very weak to weak; V.W.=Very weak.

This analysis of intensities would therefore appear to support the idea, to which reference has already been made, of stable and practically identical scattering systems for each molecule of methane throughout the structure, the molecules being arranged upon a face-centred lattice. It is difficult to interpret in any other way the fact that the most satisfactory agreement of intensities is obtained when $u=0$.

In any case, this investigation confirms the conclusion arrived at by Wahl, by optical methods, that a cubic form of methane really exists, and it disproves the view recently expressed in several papers that the structure of the methane molecule cannot be cubic, but that it must be pyramidal. No evidence of the existence of a pyramidal modification has been found in this work, but its probable existence is not disputed.

The chief arguments put forward in opposition to the existence of a cubic structure for methane have been classified by V. Henri (8) under the following heads :—

(1) The scattering of light by methane (studied by Cabannes).
(2) Its absorption spectrum (examined by Cooley and Dennison).
(3) The emission spectra of the carbon atom (examined by Millikan and Bowen).
(4). The crystal structure of methane derivatives (in particular penta-erythritol, examined by Mark and Weissenberg, and Huggins and Hendricks).
(5) Calculation of the potential energy of the methane molecule (made by Guillemin, and Van Arkel and De Boer).

If it is admitted that methane can exist in two different modifications, it is surely quite impossible to predict which of these forms is assumed for the particular conditions of experiment in cases (1) and (2). In either case the experimental technique is very difficult, and it is even possible that both forms exist together under such conditions. And in case (4) the selection of pentaerythritol as a substance whose structure might be characteristic of that of methane seems rather unfortunate in view of the fact that regular modifications of its more closely-related compounds, carbon tetrachloride, tetrabromide, and tetraiodide, are known to exist, especially as carbon tetrachloride has been shown to possess only a negligible dipole moment. The calculation of the potential energies of the pyramidal and tetrahedral configurations of the methane molecule in case (5) involves the use of the numerical data obtained from the work on the absorption spectrum in (2), and the authors of the two papers⁽⁹,¹⁰⁾ dealing with this subject are in disagreement as to which is the more stable configuration, owing to differences in original assumptions. With regard to case (3), it has been shown, by examination of the emission spectra of the carbon atom, that in neutral carbon the four valencies are not equal, but that there are two (2, 2) and two (2, 1) electrons. In methane, however, if the four electrons belonging to the hydrogen atoms join these four, and form a stable system of eight (similar to the neon electron configuration), as the analysis of intensities in this paper would seem to indicate, this objection to the existence of a cubic modification is removed. The results of this investigation therefore leave little doubt that a regular form of methane does actually exist, and this conclusion is supported by the recent work of Weissenberg⁽¹¹⁾, who has shown from theoretical considerations that for substances of the type $C\alpha_4$ the occurrence of the electrically symmetrical molecule is to be expected just as frequently as that of the pyramidal type.

A complete list of references to papers dealing with this subject is unnecessary, as excellent lists have already been prepared by the authors of the following papers:—

K. Lonsdale (*née* Yardley), Phil. Mag. vi. p. 433 (1928).
J. K. Morse, Proc. Nat. Acad. Sci. xiv. (Feb. 1928).

Note.—Though my collaborator has kindly signified that he wishes my name to be associated with this paper, I desire to say the details have been practically all worked out by him. The research is one of a number I planned and initiated, but the growing pressure of other investigations precluded my following up the work as closely as I was able to do in the early stages. I should add that throughout we had much valuable help from Mr. J. O. Wilhelm in the liquefaction of air and hydrogen. The investigation is one of the many made possible with the cryogenic equipment secured through the help of the Carnegie Corporation, the National Research Council of Canada, and the University of Toronto.—J. C. McLENNAN.

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(5) Smithsonian Tables, p. 203.

(6) H. Mark, 'Die Verwendung der Röntgenstrahlen in Chemie und Technik,' p. 474.
(7) M. Ponte, Phil. Mag. iii. p. 195 (1927).
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(9) V. Guillemin, jr., *Ann. der Physik*, (4) lxxxi. p. 173 (1926).
(10) Van Arkel and De Boer, *Zeitsch. für Physik*, xli. p. 27 (1927).
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XCIII. *The E.M.F. of Thermal Agitation.* *By* E. K. Sandeman, *Ph.D.*, *and* L. H. Bedford, *M.A.*[*]

As an incident in a certain investigation carried out for the Laboratories of the International Standard Electric Corporation, some work of J. B. Johnson on the e.m.f. of thermal agitation (Physical Review, vol. xxxii., July 1928, pp 97–109) has been verified. The accuracy of the results is not so great as his, but it is thought that the confirmatory evidence obtained is of value.

A simple precision formula has been derived, which it is believed will prove useful for many practical purposes in calculating quickly and accurately in R.M.S. microvolts the magnitude of noise disturbance which occurs on the grid of the first stage of any amplifier. This formula is admittedly only applicable under certain limiting conditions, but fortunately those limiting conditions are the ones which occur most often in practice. In practice it is usually required to amplify uniformly a given band of frequencies, and the impedance between the grid and filament of the first valve is usually a pure resistance shunted by a capacity, within the pass-band of the system The truth of this has been verified for audio-frequency systems using good input transformers to the grid of the first stage.

With the above qualifications the noise in microvolts on the grid of the first valve is given by:—

$$N=\frac{JT^{\frac{1}{2}}}{\sqrt{2\pi C}}\sqrt{\tan^{-1}2\pi RCF_2-\tan^{-1}2\pi RCF_1} \quad . \quad (1)$$

(the inverse tangents being expressed in radians), where

---

[*] Communicated by the Authors.

$J = 7{\cdot}4 \times 10^{-6}$ a constant,

T = the absolute temperature, normally about 293,

R = the total grid-filament resistance in ohms ($=$ reciprocal of sum of conductance external and internal to the valve),

C = the total grid-filament capacity in farads,

F_1 and F_2 = the frequency limits of the pass range of the receiving system in cycles per second.

J is derived directly from Boltzmann's constant K by the formula

$$J = 200\sqrt{10K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Taking the accepted value of K (Int. Crit. Tables, v. 1, p. 18) as $1{\cdot}372 \times 10^{-16}$,

$$\begin{aligned} J &= 200 \times 10^{-8} \times \sqrt{13{\cdot}73} \\ &= 7{\cdot}4 \times 10^{-6}. \end{aligned}$$

Example.

$T = 293$,

$R = 100{,}000$ ohms,

$C = 150$ micro-microfarads,

$F_1 = 30$ cycles per second,

$F_2 = 7000$ cycles per second,

$$N = \frac{7{\cdot}4 \times 10^{-6} \times 17{\cdot}1}{\sqrt{150 \times 10^{-12} \times 6{\cdot}28}} \sqrt{\tan^{-1} 6{\cdot}28 \times 10^{5} \times 150 \times 10^{-12} \times 7000 - \tan^{-1} 6{\cdot}28 \times 10^{5} \times 150 \times 10^{-12} \times 30}$$

$$\begin{aligned} &= 4{\cdot}12 \times \sqrt{\tan^{-1} 0{\cdot}66 - \tan^{-1} 0{\cdot}00283} \\ &= 4{\cdot}12 \times \sqrt{0{\cdot}584 - 0{\cdot}00283} \\ &= 4{\cdot}12 \times 0{\cdot}76 \\ &= 3{\cdot}1 \text{ microvolts (slide rule).} \end{aligned}$$

It is here evident that the second term under the root is negligible. If the value of R is increased indefinitely, the first term approaches a limiting value asymptotically and the second term also approaches the same value, lagging behind the first. The result is that as the resistance is increased indefinitely the potential variation across the resistance due to the thermal agitation increases to a maximum and then decreases. This effect is shown very well in Johnson's fig. 5 (Physical Review, July 1928, p. 103). In our experiments, owing to the low value of F_1 the lower cut-off of the amplifier system, we never reached such a maximum even by increasing R to the grid-filament conductance of the valves (about 50 megohms).

Apparatus.

The equipment consisted of a four-stage resistance-coupled amplifier using 4102–E ($\mu = 30$) valves, followed by a three-stage coil-coupled amplifier giving substantially uniform amplification in the range 30–7000 cycles. The gain of the last amplifier was adjustable in steps of 3 decibels, and was used on about half gain.

The working amplification was about two million on a voltage basis from the grid of the first valve to the plate of the last. The output was observed by means of a rectifier valve and a milliammeter, the input to the rectifier containing a potentiometer adjustable in steps of 2 decibels.

The first stage of the system was mounted on a small wooden platform slung on rubber bands in a tea-box to eliminate vibration. The foil of the tea-box afforded screening. Acoustic quietness was secured by conducting the experiments in the country, and sufficient freedom from electrical pick up was obtained by switching off the light circuit at the main.

A calibrating voltage of 1000 cycles was applied from a reed oscillator, its output being measured by a thermocouple and applied to a 600 ohm attenuator, variable in steps of 0·2 β1. The output from the attenuator was connected to a transition network having the ratio 600 : 3 ohms, and the voltage output from this was applied to the grid of the first valve through a balanced shielded coil (SS. 5115–1 Repeating Coil made by Messrs. Standard Telephones and Cables). We have found this coil invaluable for this kind of work, as it is balanced to a very high degree of accuracy, and its transmission characteristics from 30 to 10,000 cycles are excellent, *e. g.*, when operating in a 600-ohm circuit the loss in this range does not exceed 1½ decibels. As used in the circuit here described the loss was quite negligible. The stray field of such coils is also small, as they are toroidally wound, but with magnifications of the order used it was necessary to separate the input coil from the coils in the second amplifier by about fifteen feet to reduce the effects of reaction. As the circuit was originally set up to obtain comparative noise figures on different valves the presence of reaction was not serious, and it was only when idle curiosity prompted us to see how near our value of Boltzmann's constant came to the correct value that we took steps to get a better value by eliminating sources of error.

The method of measurement was to insert any value of input resistance, adjust the gain to give a convenient deflexion on the output meter, and then decrease the rectifier sensitivity by 10 decibels on its potentiometer before applying the calibrating voltage, which was adjusted until the same deflexion was again obtained. The second deflexion was therefore due to the calibrating voltage C plus the noise voltage N_1, and this deflexion corresponds to a voltage V_c, which is 10TU above N_1

$$\therefore \quad V_c = \sqrt{N_1^2 + C^2 = 3{\cdot}16\ N_1}$$

$$\therefore \quad N_1 = \frac{1}{3}\,C \text{ instead of } \frac{1}{3{\cdot}16}\,C,$$

which was the original assumption made, and would be the case if the noise voltage were eliminated while the calibrating voltage was being applied. The correction was not considered worth while taking account of at first, but the accuracy of our results, which, it must be admitted, surprised us, is such as to warrant it being applied. The observed values of J tabulated below must therefore be multiplied by $\frac{3{\cdot}16}{3}$ to give the corrected figure.

As in Johnson's work, the plate noise has been subtracted from the total observed noise results before recording them as N. The plate noise was very nearly equivalent to one microvolt on the grid and is subtracted from N_1 by taking the square root of the difference of the squares to give N.

Example of Determinations of J.

Valve 4102–E Serial No. S. 45.

Room temperature = 20° C. = 293° K.

$C = 116\mu\mu F$ (measured on a capacity and conductance bridge) + the estimated capacity of the leads $15\mu\mu F$. $= 131\mu\mu F$.

F_2 = approximately 7000 p.p.s.

F_1 = approximately 30 p.p.s.

The second term under the root may be neglected, so that the exact value of the lower cut-off of the amplifier is here unimportant. Examination of the formulæ shows that it is also very insensitive to variations of F_2, while errors in C are halved.

$$\frac{T}{\sqrt{2\pi C}} = \frac{17{\cdot}13}{\sqrt{2\pi \times 131 \times 10^{-12}}} = 597 \times 10^{-6}.$$

The remainder of the results and calculation may conveniently be tabulated :—

R.	N.	$\operatorname{Tan}^{-1} 2\pi RCF_2$.	$\sqrt{\operatorname{Tan}^{-1} 2\pi RCF_2}$.	$J \times 10^6$.
10^4	·895	·0576	·24	6·25
$5{\cdot}5 \,.\, 10^4$.	2·19	·303	·55	6·66
10^5	2·5	·523	·723	5·8
$2{\cdot}5 \,.\, 10^5$	3·72	·963	·982	6·33
$6{\cdot}10^5$	4·8	1·29	1·135	7·1
10^6	5·1	1·39	1·18	7·23

In the table below are given three sets of observed values of $J \times 10^6$:

(*a*) From measurements made on four valves with circuit as originally set up (*i. e.*, with a small amount of reaction present).

(*b*) From measurements made on one valve after steps had been taken to reduce the reaction.

(*c*) As (*b*), but with a filter inserted in the receiving system having a cut-off at 2200 cycles per second.

		a.				*b.*	*c.*
R.	Valve	4102–E	4102–E	102–E	102–E	102–E	102–E
		S. 45	S. 48	E.	B.	B.	B.
10^4		6·25	7·00	7·00	8·00	—	—
$5{\cdot}5 \,.\, 10^5$		6·66	7·66	7·80	3·50	6·22	5·70
10^5		5·80	7·10	7·28	7·70	8·20	8·40
$2{\cdot}5 \,.\, 10^5$		6·33	6·27	6·60	6·76	7·10	7·90
$6{\cdot}10^5$		7·10	5·63	6·12	5·77	6·97	7·20
10^6		7·23	5·50	6·02	5·30	—	—
Averages		6·52				7·1	7·3
Averages $\times \frac{3{\cdot}16}{3}$ ..		6·86				7·47	7·7
Derived value of Boltzmann's constant $\times 10^{16}$.		1·17				1·39	1·48

The correct value of Boltzmann's constant has already been quoted as $1·372 \times 10^{-16}$.

The improved value of Boltzmann's constant given under (*b*), obtained after steps had been taken to reduce reaction, was distinctly encouraging, and prompted us to make some effort to locate the upper cut-off more certainly. For this purpose a filter having an upper cut-off at 2200 cycles was introduced between the output of this amplifier and the rectifier. It was, however, unbalanced and unscreened, and introduced considerable reaction. Screening reduced the reaction very largely, but it is possible that reaction still persisted due to the unbalance. It will be appreciated that we were more interested in the practical confirmation of the existence of the e.m.f. of thermal agitation than in a precise determination of a constant which was already known. We considered that the above results in conjunction with those immediately below were sufficient evidence for our purpose, and it was for this reason we did not press investigation further.

As an additional check, the effect of cooling a number of grid leaks with liquid air was tried. The results are given below, the values of microvolts on the grid being completely corrected as described above. The grid leak was connected to the input of the first valve by long leads,

Effect of Cooling Grid Leaks with Liquid Air.

Type of Grid Leak.	Temperature. Centigrade.	Resistance. Megohms.	Observed microvolts.	Reduction Ratio.	Remarks.
Davohm	20°	·95	3·29	1·48	Wire wound.
„	−180	·93	2·22		
Mullard	20	1·18	3·25	1·42	
„	−180	3·9	2·35		
Western Electric.	20	·40	3·27	1·73	
	−180	·67	1·89		
Lynch	20	·53	3·55	1·5	
„	−180	·89	2·37		
Ediswan	20	1·05	4·13	1·53	
„	−180	2·92	2·69		
Dumetohm (1)	20	·94	3·51	1·67	
„	−180	1·87	2·11		
Dumetohm (2)	20	·24	3·33	1·42	Gave same value on warming up after cooling.
„	−180	·48	2·35		
Dumetohm (3)	20	·665	3·92	1·61	
„	−180	1·015	2·43		

and placed in a test-tube which was lowered into a Dewar flask containing liquid air. The Dewar flask was placed inside the tea-box which held the first stage of the amplifier.

If the observed potential variation is due to thermal agitation, then it would seem reasonable to expect that its value would be proportional to the square root of the absolute temperature (since energy is proportional to the absolute temperature and to voltage squared). In this case the expected reduction ratio in the absence of other sources of potential variation

$$=\sqrt{\frac{273+20}{273-180}}=1{\cdot}775.$$

In every case the observed reduction is less than this value. One possible explanation of this would be given by the presence of Johnson noise in the grid filament conductance of the valve itself (which was not cooled), which, adding to the noise in the resistance, makes the reduction on cooling appear smaller. Another and more obvious explanation, which, however, is not applicable in the case of the wire wound (Davohm) resistance, is that the value of the resistance increases on cooling. The diminution in reduction ratio due to this is, however, small. When $R=50{,}000$ ohms, $C=100$ micro-microfarads, $F_1=30$ cycles, and $F_2=7000$ cycles, the increase in N by doubling R, as given by equation (1), is 1·09 times. It is unfortunate for this theory that the value of reduction ratio with the wire-wound resistance was the smallest observed.

Appendix I.

Derivation of formula for N, *the potential difference generated across the terminals of a resistance* R *shunted by a capacity* C *due to the E.M.F. of thermal agitation.*

The potential difference required differs from the E.M.F. on account of the load constituted by the inevitable capacity. This load is a function of frequency, and to handle the problem it is necessary to consider the noise E.M.F. as made up of a great number of small frequency bands; the noise E.M.F. in the range of angular frequency n_1 to n_2 is therefore written,

$$e=\int_{n_1}^{n_2} E_n \cos nt \,.\, dn \qquad (n_2>n_1).$$

Lemma.

Each elemental frequency band contributes to the mean square voltage just like a distinct frequency,

i. e. $$d(\overline{E^2})=(\Delta E)^2,$$

where the left-hand side is the increment of mean square voltage corresponding to an increment dn in angular frequency, and the right-hand side is the square of the R.M.S. voltage in angular frequency range n to $n+dn$.

By the mean square voltage is meant the non-oscillating part of

$$\left(\int_{n_1}^{n_2} E_n \cos nt\, dn\right)^2.$$

This $$=\int_{n_1}^{n_2} dn \int_{n_1}^{n_2} dn' E_n E_n' \cos nt \cos n't,$$

$$=\int_{n_1}^{n_2} dn \int_{n_1}^{n_2} dn' \tfrac{1}{2} E_n E_n' (\cos \overline{n+n'}t + \cos \overline{n-n'}t).$$

To write down the non-oscillating part it is necessary to select the contributions of zero frequency; such contributions occur only when $n'=n$. Putting in this condition we find that the non-oscillating part of the mean square voltage is given by

$$\overline{E^2}=\int_{n_1}^{n_2} \tfrac{1}{2} E_n^2 dn^2.$$

But $\frac{1}{2}E_n^2 dn^2$ is the square of the R.M.S. voltage in the frequency range n to $n+dn$, which is by definition $(\Delta E)^2$.

$$\therefore\quad \overline{E^2}=\int_{n_1}^{n_2} (\Delta E)^2,$$

and $$d\overline{E^2}=(\Delta E)^2.$$

Applying this to the case of Johnson noise, Johnson states that the mean square E.M.F. of thermal agitation is uniformly distributed throughout the frequency spectrum, and that it is proportional to the absolute temperature and to the resistance in which it occurs—that is,

$$\overline{E^2}=J^2TRF,$$

where F is the width of the frequency band.

Thus $$d\overline{E^2}=J^2TRdF$$

and so $$(\Delta E)^2=J^2TRdF.$$

Now let ΔN represent the p.d. across the terminals of the resistance R due to the E.M.F. ΔE. We have,

$$\Delta N = \Delta E \frac{\frac{1}{nC}}{\sqrt{R^2 + \frac{1}{n^2C^2}}},$$

and $$N^2 = \int d(N^2) = \int (\Delta N)^2$$

$$= \int (\Delta E)^2 \frac{\frac{1}{n^2C^2}}{R^2 + \frac{1}{n^2C^2}}$$

$$= J^2TR \int_{F_1}^{F_2} \frac{\frac{1}{n^2C^2}}{R^2 + \frac{1}{n^2C^2}} dF$$

$$= J^2TR \int_{F_1}^{F_2} \frac{1}{1 + 4\pi^2C^2R^2F^2} dF$$

$$= \frac{J^2T}{2\pi C}\left[\tan^{-1} 2\pi CRF_2 - \tan^{-1} 2\pi CRF_1\right].$$

$$\therefore \quad N = \frac{JT^{\frac{1}{2}}}{\sqrt{2\pi C}} \sqrt{\tan^{-1} 2\pi CRF_2 - \tan^{-1} 2\pi CRF_1}.$$

APPENDIX 2.

Relation between Constant J *as used here and Boltzmann's Constant* K.

Nyquist (Physical Review, July 1928, p. 112, Eqn. 1) gives the relation $E^2d\nu = 4KTRd\nu$, where $E^2d\nu$ is the square of the E.M.F. corresponding to a frequency band of width $d\nu$, the quantity expressed by us as $(\Delta E)^2$.

$$E^2 d\nu = (\Delta E)^2 = J^2TRd\nu.$$

$$\therefore \quad 4KTRd\nu = (\Delta E)^2 J_1{}^2 TRd\nu,$$

where $J_1{}^2$ is the numerical value of J^2 expressed in units consistent with K being expressed in ergs per degree. J^2 as usual here is expressed in micro-micro joules per degree, so that $J^2 = 10^5$, $J_1{}^2 = 10^5 . 4K$.

$$\therefore \quad J = 200\sqrt{10K}.$$

XCIV. *Two-dimensional Periodic Orbits in the Field of a Non-Neutral.* By M. A. Higab, *M.Sc., Ph.D., Lecturer in Applied Mathematics in the Egyptian University, Cairo* *.

THE two-dimensional motion of a charged particle in the field of an electric doublet has recently been discussed by Dr. D. Wrinch (Phil. Mag. xliii. pp. 923–1014, 1923). In this discussion the only periodic orbits obtained have been semicircular; otherwise the path has always been non-periodic.

Sir G. Greenhill (Phil. Mag. xliv. pp. 372–376, 1923) has suggested the discussion of possible closed orbits, and it is the object of this paper to establish the existence and study the nature of these orbits.

The equations of motion are as follows. Let $r = \mathrm{OP}$ be the distance of the electron from O the centre of the doublet, and θ the angle which OP makes with the axis of the doublet, then

$$\ddot{r} - r\dot{\theta}^2 = -\frac{\mu}{r^2} - 2\lambda\cos\theta, \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = -\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where λ and μ are the doublet strength and central force constant, respectively, both being positive.

Equation (2) gives at once

$$r^4\dot{\theta}^2 = \mathrm{A} + 2\lambda\cos\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is a constant.

Two types of motion will be discussed separately, viz.:

(*a*) Circular motion defined by $r = \text{constant}$;

(*b*) General motion where all the coordinates vary.

Circular Motion.

Let $r = a$, where a is a constant. Equations (1) and (3) are identical if $\mathrm{A} = \mu a$.

Therefore we get

$$a^4\dot{\theta}^2 = \mu a + 2\lambda\cos\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

Since the left-hand side of equation (3′) is positive, the right-hand side must also be positive, and the following cases arise :—

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* Communicated by Prof. A. M. Mosharrafa.

(a) $\mu a > 2\lambda$. The electron goes round and round in circles. The time of one complete revolution is given by

$$T = \frac{4a^2}{\sqrt{\mu a + 2\lambda}} F\left(\frac{\pi}{2}, \sqrt{\frac{4\lambda}{\mu a + 2\lambda}}\right).$$

(b) $\mu a = 2\lambda$. The electron takes an infinite time to reach the axis $\theta = +\pi$ or $\theta = -\pi$.

(c) $0 < \mu a < 2\lambda$. The electron oscillates in an arc of a circle whose amplitude is greater than $\pi/2$ and bounded by the lines

$$\theta = \pm\left[\pi - \cos^{-1}\frac{\mu a}{2\lambda}\right].$$

The periodic time is given by

$$T = \frac{4a^2}{\sqrt{\lambda}} F\left(\frac{\pi}{2}, \sqrt{\frac{\mu a + 2\lambda}{4\lambda}}\right).$$

(d) $\mu = 0$. The electron oscillates in a semicircle between the lines $\theta = \pm\pi/2$. The periodic time is given by

$$T = \frac{4a^2}{\sqrt{\lambda}} F\left(\frac{\pi}{2}, \frac{1}{\sqrt{2}}\right).$$

This is the case discussed by Dr. D. Wrinch.

GENERAL MOTION.

Since the left-hand side of equation (3) is positive, the right-hand side must also be positive. Therefore A cannot be less than -2λ, and the following cases arise :—

(a) $A > 2\lambda$. In this case $A + 2\lambda\cos\theta$ is always positive, and the motion is not restricted as regards θ. Also the transverse velocity of the electron does not vanish in the finite part of the plane.

(b) $A = 2\lambda$. Here the lines $\theta = \pm\pi$ cannot be crossed.

(c) $0 < A < 2\lambda$. The lines $\theta = \pm\left[\pi - \cos^{-1}\frac{A}{2\lambda}\right]$ cannot be crossed. The angle which defines the region of motion in this case is twice an obtuse angle.

(d) $A = 0$. The lines $\theta = \pm\pi/2$ cannot be crossed.

(e) $0 > A > -2\lambda$. The lines $\theta = \pm \cos^{-1}\frac{|A|}{2\lambda}$ cannot be crossed. The angle which defines the region of motion in this case is twice an acute angle.

(f) $A = -2\lambda$. The motion is along the axis $\theta = 0$.

N.B.—The only cases which give rise to periodic orbits are (a) and (c), so we shall be concerned with their discussion only. In every other case the path is non-periodic.

The Differential Equation of the Path.

Eliminating $\dot{\theta}$ between equations (1) and (3), we get:

$$\ddot{r} = -\frac{\mu}{r^2} + \frac{A}{r^3},$$

the first integral of which is

$$\dot{r}^2 = \frac{2\mu}{r} - \frac{A}{r^2} + B,$$

where B is a constant.

If we put $u = \frac{1}{r}$ and write $\frac{du}{d\theta} = u_1$ we obtain for the differential equation of the path:

$$(A + 2\lambda \cos\theta) u_1^2 = 2\mu u - Au^2 + B, \quad . \quad . \quad . \quad (4)$$

where $(A + 2\lambda\cos\theta)$ is necessarily positive.

Case (a).

$A > 2\lambda$. In equation (4), since $A \neq 0$, we can divide by it and get

$$\left(1 + \frac{2\lambda}{A}\cos\theta\right) u_1^2 = \frac{e^2}{l^2} - \left(u - \frac{1}{l}\right)^2, \quad . \quad . \quad . \quad (5)$$

where

$$\frac{B}{A} + \frac{\mu^2}{A^2} = \frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu}{A} = \frac{1}{l}.$$

Now

$$u_1 = 0 \quad \text{at} \quad u = \frac{1 \pm e}{l}.$$

Three different cases arise :—

(1) $e < 1$. In this case r oscillates between the maximum

and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively, and the motion is included between the two circles

$$r=\frac{l}{1-e} \quad \text{and} \quad r=\frac{l}{1+e}.$$

The radial velocity vanishes on each of these two circles.

Integrating equation (5) we obtain for the equation of the path

$$\frac{l}{r}=1+e\cos\left[c+2\sqrt{\frac{A}{A+2\lambda}}F\left(\psi,\sqrt{\frac{4\lambda}{A+2\lambda}}\right)\right., \quad (6)$$

where c is a constant and $\psi=2\theta$.

For different values of the constant (c) and the modulus $\sqrt{\frac{4\lambda}{A+2\lambda}}$, equation (6) represents a series of curves which may or may not be periodic.

The condition for periodicity is

$$\int_0^{k\pi}\frac{d\psi}{(1-x\sin^2\psi)^{1/2}}=m\pi\sqrt{\frac{2}{2-x}}, \quad . \quad . \quad (7)$$

where

$$x=\frac{4\lambda}{A+2\lambda},$$

and k and m are positive integers.

Corresponding to each pair of positive integers (k, m), a definite value of x may be obtained such as to satisfy equation (7), and the three parameters (k, m, x) will then define a type of periodic orbit. We shall find it convenient to speak of types of class ($m-k+1$) and order k. In all orbits of order k the motion is represented at $\psi=k\pi$. In this paper typical solutions of equation (7) for pairs of integers have been obtained graphically; the following results have been obtained:—

Types of the First Order, $k=1$.

Orbits of class (1) are given by

$$m=1, \quad x=0, \quad \lambda=0.$$

All orbits of this type are ellipses.

Orbits of class (2) are given by

$$m=2, \quad x=\cdot 998, \quad \frac{A}{\lambda}=2\cdot 007.$$

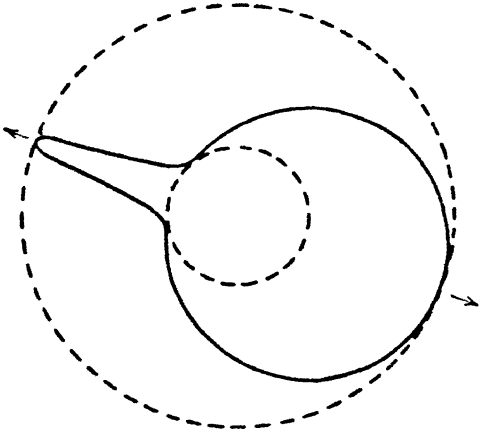
Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in four points.

Orbits of class (3) are given by

$$m=3, \quad x=\cdot 9999, \quad \frac{A}{\lambda}=2\cdot 0004.$$

Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in six points.

Fig. 1.



In general, types of order (I.) and class S are given by $m=S$, and the number of points of tangency to the circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ is 2S.

Theoretically speaking, there are an infinite number of orbits in this class, but as A gets nearer and nearer to 2λ, the electron oscillates closer and closer to the axis $\theta=\pi$.

A typical orbit of class (1) and order (I.) is shown in fig. 1.

Types of the Second Order, $k=2$.

Orbits of class (1) are given by

$$m=2.$$

These orbits are of class (1) and order (I.) described twice.

Orbits of class (2) are given by

$$m=3, \quad x=\cdot 9781, \quad \frac{A}{\lambda}=2\cdot 08966.$$

Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in six points.

Orbits of class (3) are given by

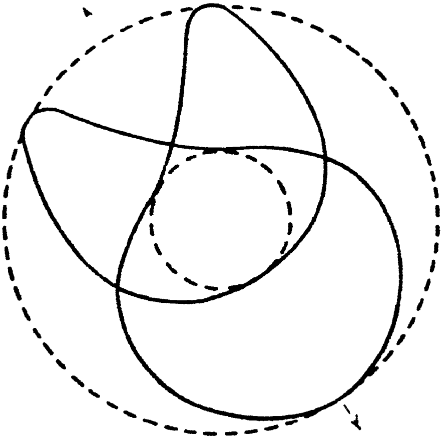
$$m=4.$$

These orbits are of class (2) and order (I.) described twice.

Orbits of class (4) are given by

$$m=5, \quad x=\cdot 9998, \quad \frac{A}{\lambda}=2\cdot 0019.$$

Fig. 2.



Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in ten points.

In general, types of order (II.) and class S are given by $m=S+1$. If $S+1$ is even, this orbit is that of class $\left(\frac{S+1}{2}\right)$ of the first order described twice; but if $S+1$ is odd, then this is the S periodic of the second order, and the number of points of tangency to the two circles is $2S+2$.

A typical orbit of class (2) and order (II.) is shown in fig. 2.

Generally the periodic orbits of order t and class S are given by $k=t$, $m=\mathrm{S}+t-1$, x being a root of the equation

$$t\mathrm{F}\left(\frac{\pi}{2},\ \sqrt{x}\right)=\frac{m\pi}{2}\sqrt{\frac{2}{2-x}}.$$

If m and t are not prime to one another, then these orbits will be orbits of a lower order multiply described.

(2) $e=1$. The outer circle becomes infinite, and r passes through the minimum value $l/2$ and extends to infinity. Thus the motion is outside the circle $r=l/2$. The path in this case touches the circle at infinity.

(3) $e>1$. The outer circle does not exist, and r passes through the minimum value $\frac{l}{1+e}$. Thus the motion is outside the circle $r=\frac{l}{1+e}$. The path in this case proceeds to infinity along asymptotes.

Case (c).

$0<\mathrm{A}<2\lambda$. The differential equation of the path is

$$\left(1+\frac{2\lambda}{\mathrm{A}}\cos\theta\right)u_1{}^2=\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2, \quad . \quad . \quad . \quad (8)$$

where

$$\frac{\mathrm{B}}{\mathrm{A}}+\frac{\mu^2}{\mathrm{A}^2}=\frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu}{\mathrm{A}}=\frac{1}{l}.$$

Now

$$u_1=0 \quad \text{at} \quad u=\frac{1\pm e}{l}.$$

Three different cases arise :—

(1) $e<1$. In this case r oscillates between the maximum and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively, and the motion is included between the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$. Integrating equation (8) we get the equation of the path to be

$$\frac{l}{r}=1+e\cos\left[c+\sqrt{\frac{\mathrm{A}}{\lambda}}\,\mathrm{F}\left(\psi,\ \sqrt{\frac{\mathrm{A}+2\lambda}{4\lambda}}\right)\right. \quad . \quad (9)$$

For different values of the constant c and the modulus $\sqrt{\frac{A+2\lambda}{4\lambda}}$, equation (9) represents a series of curves which may or may not be periodic.

The condition for periodicity is

$$\int_0^{k\pi} \frac{d\psi}{(1-x\sin^2\psi)^{1/2}} = \frac{2m\pi}{\sqrt{4x-2}}, \quad . \quad . \quad . \quad (10)$$

where $$x = \frac{A+2\lambda}{4\lambda}$$

and $$\psi = \sin^{-1}\left[\sqrt{\frac{A+2\lambda}{4\lambda}}\sin\frac{\theta}{2}\right],$$

and k and m are positive integers.

Equation (10) has been solved graphically and the following results obtained :—

Types of Order (I.), $k=1$.

Orbits of class (1) are given by

$$m = 1, \quad x = \cdot 8851, \quad \frac{A}{\lambda} = 1\cdot 5404.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in three points.

Orbits of class (2) are given by

$$m = 2, \quad x = \cdot 999, \quad \frac{A}{\lambda} = 1\cdot 99.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in five points.

Theoretically speaking, there are an infinite number of orbits of this order, but as A gets nearer to 2λ, the electron oscillates nearer the axis $\theta=\pi$.

A typical orbit of class (1) and order (I.) is shown in fig. 3.

Types of Order (II.), $k=2$.

Orbits of class (1) are given by

$$m = 1, \quad x = \cdot 6411, \quad \frac{A}{\lambda} = \cdot 5644.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in two points.

Orbits of class (2) are given by

$$m = 2.$$

These are the orbits of class (1) and order (I.) described twice.

Orbits of class (3) are given by

$$m=3,\quad x=\cdot 9807,\quad \frac{A}{\lambda}=1\cdot 9228\,\lambda.$$

Fig. 3.

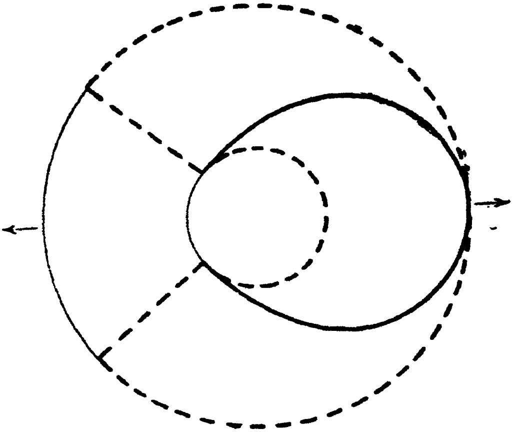
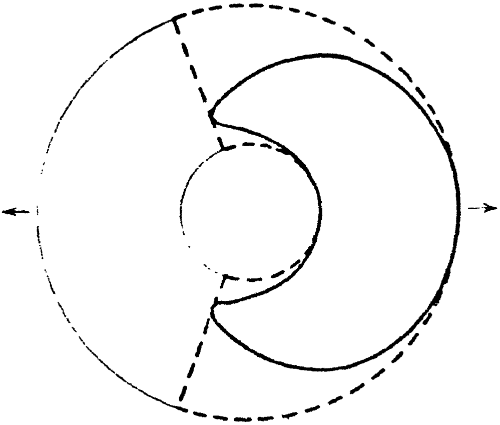


Fig. 4



Orbits of this type touch the circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in six points.

As before, there are an infinite number of orbits of this order.

A typical orbit of class (1) and order (II.) is shown in fig. 4.

Generally the periodic orbits of order t and class S are defined by $k=t$, $m=\mathrm{S}$, x being a root of the equation

$$t\mathrm{F}\left(\frac{\pi}{2},\ \sqrt{x}\right)=\frac{m\pi}{\sqrt{4x-2}}.$$

If m and t are not prime to one another, then these orbits will be orbits of lower order multiply described.

(2) $e=1$. The path is always open and touches the circle at infinity.

(3) $e>1$. The path is always open and proceeds to infinity along asymptotes.

In conclusion, I wish to express my thanks to Prof. S. Brodetsky, of Leeds University, under whose supervision the above work has been done, and to Prof. A. M. Mosharrafa for criticisms and suggestions.

SUMMARY.

The motion of a charged particle in the field of an electric doublet is discussed.

Conditions for periodic orbits are obtained, and typical examples are discussed and illustrated.

XCV. *Application of Talbot's Law to Photoelectric Cells with a Non-linear Illumination-current Characteristic.*

By G. H. CARRUTHERS, *B.Sc.*, *A.R.C.S.* (*Admiralty Research Laboratory*), *and* T. H. HARRISON, *Ph.D.*, *B.Sc.*, *A.Inst.P.* (*National Physical Laboratory*)[*].

ABSTRACT.

A SIMPLE analysis shows that Talbot's law should be valid for a cell in which the photo-electric current is proportional to the illumination, but should fail for a cell in which this proportionality does not hold. A series of careful experiments with cells for which this proportionality holds, and with others for which the proportionality fails, shows, however, that Talbot's law holds for both types.

From this is deduced an explanation as to the cause of this failure of proportionality, based on a rapid fatigue effect during the time that the cell is exposed to the illumination,

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[*] Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

and a recovery effect during the period that the cell is occulted by the sector. With a cell for which the proportionality law holds there is no such rapid fatigue and recovery.

TALBOT'S law is stated by Helmholtz as follows:—

"If any part of the retina is excited with intermittent light, recurring periodically and regularly in the same way, and if the period is sufficiently short, a continuous impression will result which is the same as that which would result if the total light received during each period were uniformly distributed throughout the whole period *."

Normally a sector disk rotating about its centre is employed to obtain the intermittent effect, and in this case Talbot's law reduces to the statement that the effective brightness of the source is proportional to the angular opening of the sector.

E. P. Hyde, who conducted a searching test of Talbot's law as applied to the eye, said that "Talbot's law is thus a statement of physiological rather than physical phenomena, and depends for its explanation on the action of the eye †.

The results of Hyde's investigations established the accuracy of Talbot's law applied to the eye with an accuracy of 0·3, which represented the limit of accuracy of experiment.

The applicability of Talbot's law to the bolometer was tested by W. W. Coblenz ‡, who found that the energy transmitted by a rotating sector disk is appreciably greater than the theoretical value. The experimental evidence showed that this increase varied with the speed of the disk and with the distance between the sector disk and the bolometer. No completely satisfactory explanation was offered for this failure of Talbot's law, but it was considered probably due to diffraction of the waves of longer wavelength.

The applicability of Talbot's law to the photoelectric cell has been tested by J. Kunz § and by H. E. Ives Dushman and Karrer ‖. In the work of Kunz the investigation was confined to one photoelectric cell for which the photoelectric current was proportional to the illumination, that is, it

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* *Physiolog Optik*, iii. Auflage, ii. p. 174.

† Bulletin of the Bureau of Standards, ii. p. 1 (1906).

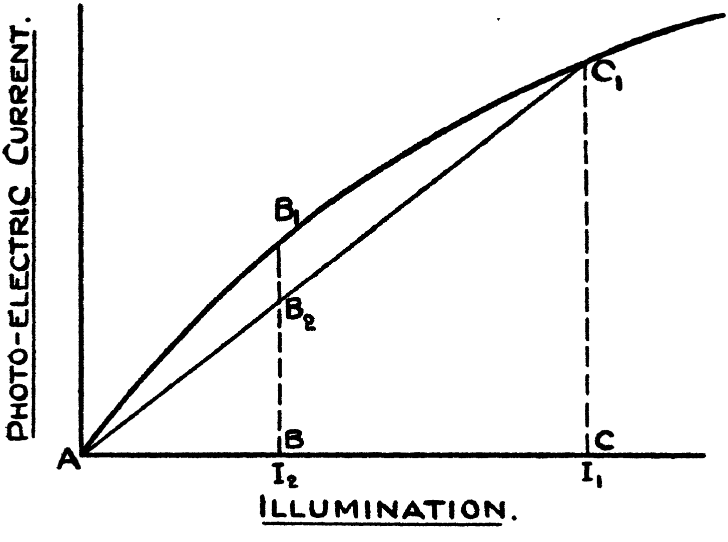
‡ Bulletin of the Bureau of Standards, iv, p. 455 (1907).

§ Astrophysical Journal, xlv. pp. 76–77 (1917).

‖ Astrophysical Journal, xliii. pp. 1–35 (1916).

possessed a linear illumination-current characteristic. The characteristic was found by varying the illumination on the cell firstly by means of crossed Nicol prisms, and secondly by means of a rotating disk with various angular apertures. Both methods of varying the illumination gave straight lines, with the same slope in each case, and from this Kunz concluded that Talbot's law holds for the photoelectric cell. Unfortunately no numerical data are given from which the accuracy of the agreement of the two methods can be obtained. Also the fact that the one cell tested, on which his conclusion is based, possessed a linear illumination-current characteristic is distinctly unfortunate, as will be seen by consideration of the following.

Fig. 1.



Consider a cell with a non-linear illumination-current characteristic, which is shown in fig. 1. When this cell is exposed to a steady illumination I_1, the photoelectric current is represented by CC_1. If the cell is exposed to steady illumination I_2, then the photoelectric current will be BB_1. Let us now consider the case in which the illumination I_1 is reduced to the value I_2 by the introduction of a sector disk of ratio I_2/I_1; then according to the usual conception of the photoelectric current by which the passage of electrons occurs almost instantaneously on exposure to light, it is reasonable to suppose that the photoelectric current CC_1

will be reduced not to the value of BB_1, but to BB_2, where B_2 lies on the straight line joining the origin to C_1, since the electrons now pass only for periods totalling I_2/I_1 per unit time. Thus, whatever the true characteristic of the cell may be, a straight-line relation will be obtained by varying the angular opening of the sector disk.

It is evident from this that the investigation of Kunz using a linear cell is by no means conclusive evidence of the validity of Talbot's law as applied to photoelectric cells in general. The same objection applies to the work of Ives, who also tested the law on a cell with a linear characteristic. Ives, however, went one step further by checking one point on the characteristic curve of a cell with a non-linear relationship. From this he also concludes that Talbot's law can be applied to photoelectric cells. No data from which conclusions can be drawn as to the amount of departure from linearity of the cell, the closeness of the agreement between the two methods, or the experimental error are given. In addition to the above investigations, an earlier test was carried out by Elster and Geitel; here again tests were carried out on cells with a linear characteristic.

In view of the unsatisfactory nature of the evidence of the applicability of Talbot's law to photoelectric cells, particularly to those with non-linear characteristics, it was decided to carry out a thorough investigation, and for this purpose specimens representing as many different types of cells as possible were collected. The collection included cells made with potassium, sodium, rubidium, cæsium, and lithium. Some were gas-filled, others were evacuated.

Preliminary experiments were tried with a Lindemann electrometer with a view to measuring the potential of the junction-point of a cell in series with a high resistance. On account, however, of a small creep in the deflexion of the needle when a constant potential was applied, it was found impossible to take observations of sufficient accuracy. Recourse was then had to an apparatus that had been previously designed by one of the authors for photometric work on principles outlined by C. H. Sharp and H. A. Smith *.

The arrangement of the apparatus is shown in fig. 2. The cathode of the cell to be tested is connected in series with a 15-megohm resistance, and the junction-point to the grid of a thermionic valve. The other end of the 15-megohm

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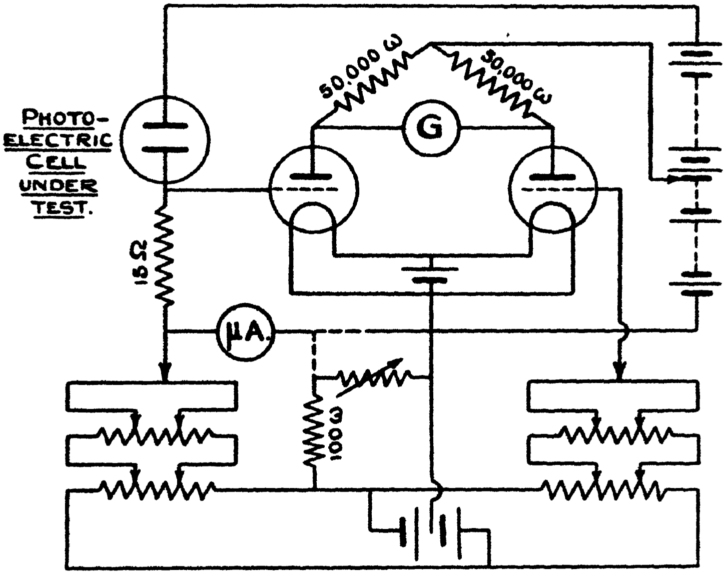
* C. H. Sharp and H. A. Smith, Trans. Ill. Eng. Society, p. 431 (New York, 23 April, 1928).

resistance is connected to the slider of a potential dividing system so that the grid of the left-hand valve can be set at any desired potential within a range of +2 volts relative to the negative end of its filament. The grid of the right-hand valve is connected directly to the slider of another similar potential divider (lower right-hand corner of the diagram). Initially the photoelectric cell is in darkness, and there is only the dark current passing through the 15-megohm leak. The grid of the left-hand valve is set at zero voltage relative

Fig. 2.



to the negative end of the filament, as indicated by the microammeter, whilst that of the right-hand valve is set at such a potential that the Wheatstone bridge formed by the two valves and the two 50,000-ohm resistance is balanced, and no current passes through the galvanometer G. If, now, the photoelectric cell is illuminated so that there is an increase in the current, the grid of the left-hand valve acquires a positive potential, and the bridge is put out of balance. The balance, however, can be restored by moving the sliders of the left-hand potential divider to which the 15-megohm leak is connected. When this is done, the grid of the left-hand valve is again at zero potential, and the microammeter, which is used as a millivoltmeter, gives a reading corresponding to the fall in potential along the grid-leak due to the photoelectric current passing through it. In this way the reading on the microammeter is directly proportional to the photoelectric current. In order to increase the range of the microammeter, another potential dividing system is used in connexion with a switch by which it is either inserted or cut out of action. No trouble was experienced through unsteadiness of the valves, but electrostatic shielding, obtained by placing all the apparatus inside an earthed metal-lined box, was essential. The photoelectric cell, behind a suitably-screened aperture in the side of the box, was exposed to the light from a 1000-watt concentrated uniplanar filament lamp mounted on a photometer bench. The size of the filament was 1·5 cm. by 1·3 cm., and the correction for size of filament was found to be negligible. To ensure that the voltage across the lamp was constant, a potentiometer was employed.

The sectors used in conjunction with the thermionic bridge were made with two equal apertures symmetrically arranged. They were carefully cut out of millboard, the centres being strengthened with brass centre-pieces which closely fitted a sleeve fixed to the shaft of a small motor. The latter, which was mounted on a separate support to avoid vibration troubles, was arranged so that the sectors were about 10 cm. in front of the cell. To test whether the response of the system was affected by any sparking from the motor, the latter was run without a sector disk, and it was found that the balance of the bridge was in no way disturbed. Each sector was calibrated, the ratio of the open to the closed part being determined to five in the fourth place of decimals. The nominal values of the ratios of the sectors were 0·75, 0·667, 0·5, 0·333, 0·25, 0·167, and the actual values agreed with these to one in the third place of decimals.

The results of the tests on six cells are given in the paper. The first set of results refers to a potassium neon cell with a wire ring anode which had been sensitized by the Elster and Geitel process. The inside of the cell was, except for the window, completely covered with the alkali metal, as is the usual practice. This cell showed a decided departure from linearity in its illumination-current characteristic, that is to say, the photoelectric current was not proportional to the illumination when this was varied by moving a lamp along a photometer bench and applying the inverse square laws. The second set of results refers to a cæsium vacuum cell with a wire ring anode, which also showed a decided departure from linearity, but its response to a given illumination was apt to vary slightly. This was probably caused by the shortness of the glass neck which separated the anode and cathode, and resulted in a dark current of slightly variable magnitude. The third set of results refers to a rubidium helium cell with a wire ring anode. With this cell, as with the cæsium cell, there was an appreciable dark current when 100 volts were applied. The fourth set of results refers to a sodium vacuum cell provided with a quartz window for use in the ultra-violet. The anode again consisted of a wire ring. Both the rubidium helium and the sodium vacuum cells show a slight departure from linearity. The fifth set of results refers to a rubidium vacuum cell. In this cell the alkali metal cathode, instead of being on the inside glass surface, as is usual, was formed on a metallic plate. The silvered inner surface of the cell formed the anode. The sixth set of results refers to a potassium neon cell made of uviol glass. In order to secure a uniform field, the anode of this cell is in the form of a grid. The two cells last mentioned showed no departure from linearity greater than that which could bo safely attributed to experimental error. Other cells were tested, in particular a lithium cell provided with a quartz window. This cell, however, which was designed for use in the ultra-violet, was so very insensitive, even to light from a quartz mercury vapour lamp, that no useful results could be obtained. This insensitivity may have been due to faulty manufacture. Three other cells were tested and, being linear, gave no additional information, and the results are not included.

In taking observations the routine adopted was first to observe the photoelectric current when the cell was exposed to a given illumination. The illumination was then reduced in a given ratio, firstly by introducing a sector disk, and secondly by moving the lamp along the photometer bench to the appropriate distance, as given by the inverse square law. Finally, as a check, and to eliminate any slow changes, the sector disk was again used, and also there was again an exposure to the full steady illumination. Between each of these operations a rebalancing of the bridge was made in case of any alteration of the zero. In order to avoid any slow changes in the response of the cell, the precaution was taken of not exposing the celi unnecessarily. With regard to the potassium cell—the first cell mentioned—an attempt was made to increase the non-linearity by raising the voltage and also the illumination. This, as was feared, resulted in arcing the cell, the inside of which seemed to be filled with a reddish glow similar to that observed in neon lamps. A subsequent determination of its illumination-current characteristic showed it to be completely changed. It was now quite linear and four times as sensitive, this increase being chiefly in the blue region. A redetermination of its characteristic six weeks later showed, however, that the cell was gradually reverting to its previous state. This may be a point of further interest in the determination of the reason of non-linearity. The results obtained immediately after the arcing of the cell are also given below.

The results obtained with the thermionic-bridge system are given in Tables I.–VII. They show that the probable error in the determination of the ratios of the photoelectric currents is 2×10^{-3}. Apart from the cæsium cell, the greatest difference shown by any of the cells tested between the inverse square result and the sector disk result was three times the probable error. It is to be concluded from the experimental results with the thermionic-bridge system that, contrary to expectation, Talbot's law holds for photoelectric cells whether their response is proportional to the illumination or not.

TABLE I.—Thermionic Bridge.

Potassium neon cell.

Diameter of window, 18 mm.

100 volts across cell.

Lamp at 60 volts, giving 490 candle-power.

Current flowing through cell for maximum illumination (605 metre candles) was $4{\cdot}0 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·764	0·687	0·523	0·356	0·271	0·184	0·093
Departure from linearity $\times 10^3$.	+14	+20	+23	+23	+21	+17	+10
Current ratio (sector disk).	0·766	0·683	0·527	0·355	0·270	0·183	
Departure from linearity $\times 10^3$.	+16	+16	+27	+22	+20	+16	
Inverse square less sector ratio $\times 10^3$.	− 2	+ 4	+ 4	+ 1	+ 1	+ 1	

TABLE II.—Thermionic Bridge.

Cæsium vacuum cell.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 55 volts, giving 350 candle-power.

Current flowing through cell for maximum illumination (432 metre candles) was $3{\cdot}4 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·765	0·691	0·521	0·361	0·272	0·188	0·100
Departure from linearity $\times 10^3$.	+15	+24	+21	+28	+22	+21	+17
Current ratio (sector disk).	0·761	0·682	0·521	0·362	0·280	0·191	
Departure from linearity $\times 10^3$.	+11	+15	+21	+29	+30	+24	
Inverse square less sector ratio $\times 10^3$.	+ 4	+ 9	0	− 1	− 8	− 3	

TABLE II *a*.—Galvanometer.

Cæsium vacuum cell.

Lamp at 77 volts, giving 1149 candle-power.

Current flowing through cell for maximum illumination (1418 metre candles) was 11×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·750	0·683	0·519	0·352	0·269	0·182	0·097
Departure from linearity $\times 10^3$.	0	+16	+19	+19	+19	+15	+14
Current ratio (sector disk).	0·755	0·680	0·516	0·350	0·272	0·185	
Departure from linearity $\times 10^3$.	+5	+13	+16	+17	+22	+18	
Inverse square less sector ratio $\times 10^3$.	−5	+ 3	+ 3	+ 2	− 3	− 3	

Table III.—Thermionic Bridge.

Rubidium helium cell.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}6 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·125
Current ratio (inverse square law).	0·757	0·670	0·507	0·340	0·255	0·174	0·129
Departure from linearity $\times 10^3$.	+7	+3	+7	+7	+5	+7	+4
Current ratio (sector disk).	0·753	0·672	0·510	0·340	0·258	0·173	
Departure from linearity $\times 10^3$.	+3	+5	+10	+7	+8	+6	
Inverse square less sector ratio $\times 10^3$.	+4	−2	−3	0	−3	+1	

Table IV.—Thermionic Bridge.

Sodium vacuum cell with quartz window.

Diameter of window, 18 mm.

100 volts across cell.

Lamp run at 60 volts, giving 490 candle-power.

Current flowing through cell for maximum illumination (605 metre candles) was $3{\cdot}4 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·756	0·670	0·505	0·341	0·257	0·172	0·087
Departure from linearity $\times 10^3$.	+6	+3	+5	+8	+7	+5	+4
Current ratio (sector disk).	0·755	0·669	0·505	0·340	0·257	0·173	
Departure from linearity $\times 10^3$.	+5	+2	+5	+7	+7	+6	
Inverse square less sector ratio $\times 10^3$.	+1	+1	0	+1	0	−1	

TABLE V.—Thermionic Bridge.

Rubidium vacuum cell, plate type.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 47 volts, giving 194 candle-power.

Current flowing through cell for maximum illumination (240 metre candles) was 4·3 × 10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·749	0·666	0·503	0·337	0·254	0·168	0·085
Departure from linearity × 10^3.	−1	−1	+3	+4	+4	+1	+2
Current ratio (sector disk).	0·747	0·666	0·498	0·333	0·253	0·162	
Departure from linearity × 10^3.	−3	−1	−2	0	+3	−5	
Inverse square less sector rati × 10^3.	+2	0	+5	+4	+1	+6	

TABLE V*a*.—Galvanometer.

Rubidium vacuum cell, plate type.

Lamp run at 71·0 volts, giving 890 candle-power.

Current flowing through cell for maximum illumination (1099 metre candles) was 19 × 10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·749	0·669	0·409	0·330	0·246	0·165	0·081
Departure from linearity × 10^3.	−1	+2	−1	+3	−4	−2	−2
Current ratio (sector disk).	0·746	0·674	0·496	0·328	0·247	0·164	
Departure from linearity × 10^3.	−4	+7	−4	−5	−3	−3	
Inverse square less sector ratio × 10^3.	+3	−5	+3	+2	−1	+1	

TABLE VI.—Thermionic Bridge.

Potassium neon cell made of uviol glass.

Anode of cell in grid form.

Diameter of cell window, 20 mm.

90 volts across cell.

Lamp run at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}2 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·752	0·668	0·504	0·334	0·251	0·167	0·083
Departure from linearity $\times 10^3$.	+2	+1	+4	+1	+1	0	0
Current ratio (sector disk).	0·750	0·668	0·500	0·330	0·251	0·166	
Departure from linearity $\times 10^3$.	0	+1	0	−3	+1	−1	
Inverse square less sector ratio $\times 10^3$.	+2	0	+4	+4	0	+1	

TABLE VII.—Thermionic Bridge.

Potassium neon immediately after arcing.

Lamp at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}7 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·755	0·668	0·502	0·336	0·253	0·168	0·085
Departure from linearity $\times 10^3$.	+5	+1	+2	+3	+3	+1	+2
Current ratio (sector disk).	·751	·667	0·500	0·333	0·253	0·166	
Departure from linearity $\times 10^3$.	+1	0	0	0	+3	−1	
Inverse square less sector ratio $\times 10^3$.	+4	+1	+2	+3	0	+2	

TABLE VII *a*.—Galvanometer.

Potassium neon after arcing.

Lamp at 55·6 volts, giving 367 candle-power.

Current flowing through cell for maximum illumination (453 metre candles) was 18×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·751	0·668	0·499	0·326	0·247	0·161	0·083
Departure from linearity $\times 10^3$.	+1	+1	−1	−7	−3	−6	0
Current ratio (sector disk).	0·748	0·666	0·499	0·325	0·247	0·161	
Departure from linearity $\times 10^3$.	−2	−1	−1	−8	−3	−6	
Inverse square less sector ratio $\times 10^3$.	+3	+2	0	+1	0	0	

TABLE VII *b*.—Galvanometer with Shunt.

Potassium neon after arcing.

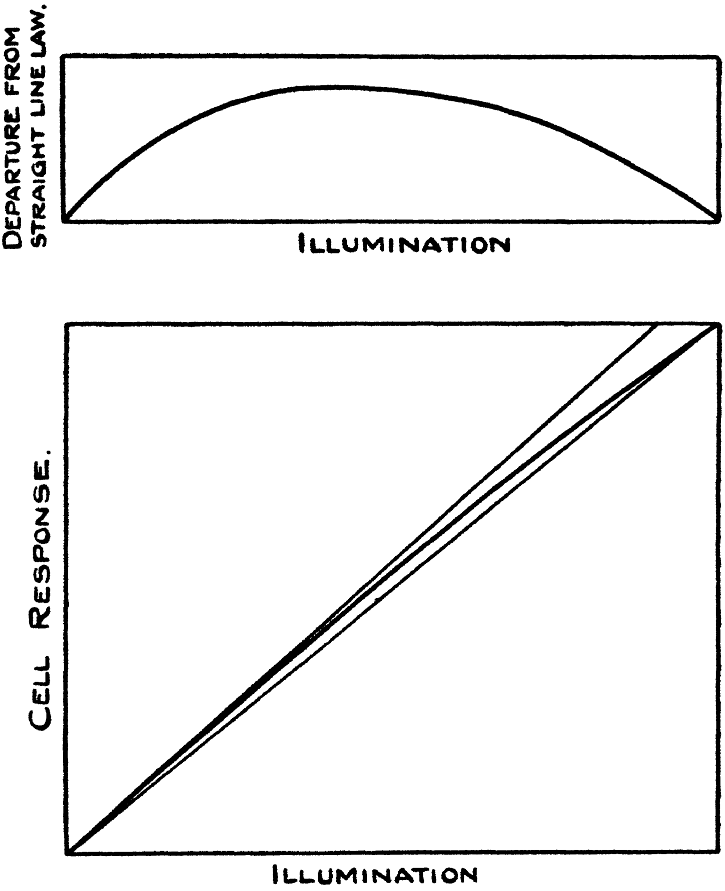
Lamp at 77 volts, giving 1149 candle-power.

Current flowing through cell for maximum illumination (1418 metre candles) was 84×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·747	0·665	0·498	0·328	0·248	0·163	0·080
Departure from linearity $\times 10^3$.	−3	−2	−2	−5	−2	−4	−3
Current ratio (sector disk).	0·749	0·669	0·500	0·331	0·250	0·164	
Departure from linearity $\times 10^3$.	−1	+2	0	−2	0	−3	
Inverse square less sector ratio $\times 10^3$.	−2	−4	−2	−3	−2	−1	

In the lower part of fig. 3 the illumination-current curve of the potassium neon cell before the glow discharge occurred is shown. The ordinates represent the photoelectric current and the abscissæ the illumination. The straight line connecting the origin with the point on the curve corresponding to the maximum illumination represents the response which, according to the argument already outlined, would be given by the cell when the illumination is varied by means of the sector. The upper part of fig. 3 represents on a large scale the difference between this straight line and the actual illumination-current curve which, since Talbot's law is obeyed, was found to be the same when the illumination was varied with sector disks as when it was varied by altering the distance of the lamp. There is also shown the tangent of the curve at the origin; this will be referred to later.

Fig. 3.



The curves for the other cells are not included, as they give no additional information.

Part of the routine test on each cell was the variation of the sector-speed over a range from about five revolutions to fifty revolutions per second. The balance of the bridge was quite unaltered by those changes of sector-speed, and this showed not only that any changes of the average response of the cell were smaller than could be detected with the apparatus, but also that the intermittent photoelectric current through the cell was being correctly integrated by the apparatus. If, for instance, such a strong illumination were employed that the change of potential at the junction of the cell and the 15-megohm resistance was so great that when applied to the grid of the valve the latter was no longer working on the straight-line portion of its characteristic, then this would be indicated by an apparent change of photoelectric current with change of sector-speed. Thus, when using intermittent illumination, there is an upper limit to the brightness of the source that may be used in conjunction with the thermionic bridge, so that in order to test the validity of Talbot's law over a wider range a simple galvanometer circuit was employed. These results are given in Tables II *a*, V *a*, VII *a*, and VII *b*, and confirm, within experimental error, those obtained with the thermionic bridge, showing that Talbot's law holds even for the highest illuminations. One thing that came out clearly in this work was that cells of the short-necked type have a very large undesirable dark current which varies from day to day. The cæsium cell was a typical example of this.

In order to investigate the validity of Talbot's law with a higher degree of precision than was obtainable using the thermionic bridge, further experiments were conducted with an apparatus which has been described in detail elsewhere*. It will be sufficient to give here a brief outline of the essential features, which are shown diagrammatically in fig. 4. Two photoelectric cells, C_1, the one to be tested, and any second cell, C_2, are connected in series with a 200-volt battery, the centre-point of which is earthed. The junction-point of the cells is connected to one pair of quadrants of a Compton electrometer E, the other pair being earthed. M is a sliding mirror by which C_1 can be illuminated either by the lamp L_1, which is fixed in position, or by the lamp L_2, which can be moved along a photometer-bench. C_2 is illuminated by a source which can be kept constant at any required value. In this case it conveniently took the form of a lamp L_3, placed in a 4-ft. cube, this being already in position in connexion with other work. Between the lamp L_1 and the mirror M a sector could be rotated, and thus reduce the effective illumination from L_1. The procedure adopted in the test was to illuminate C_1 by L_1 and C_2 by L_3, adjusting the voltage across L_3 until the photoelectric current in C_2 was equal to that in C_1. When this adjustment was made the junction-point of the cells remained at earth potential, and the electrometer needle was undeflected. The mirror M was then raised so that C_1 was illuminated by L_2 instead of L_1. The position of L_2 on the bench was then adjusted until the electrometer again showed no deflexion, and the bench-reading noted. As a check that the photoelectric current per unit illumination for both cells had remained

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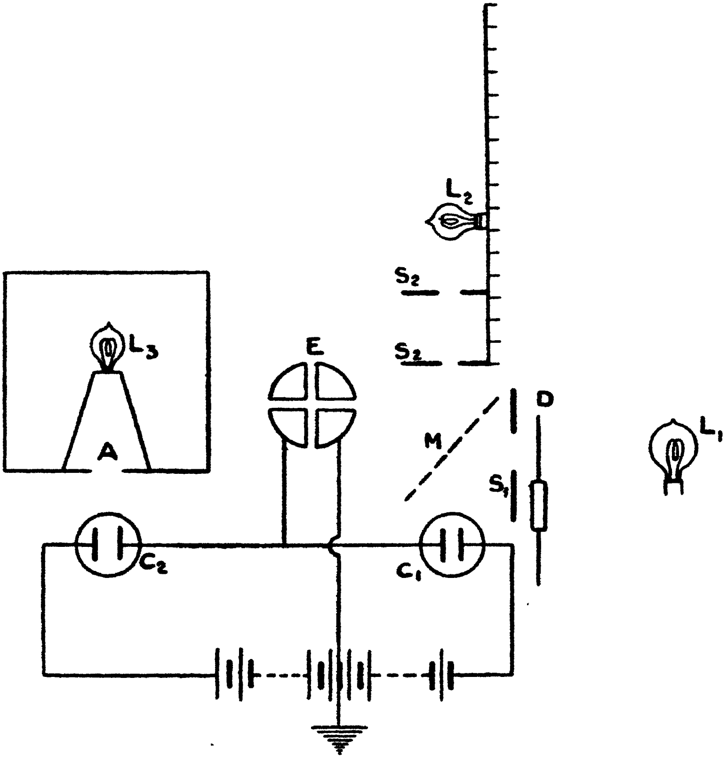
* T. H. Harrison, Proc. Opt. Convention, 1926, p. 245.

Fig. 4.



constant over the short time occupied in the last adjustment, the mirror M was lowered again so that C_1 was illuminated by L_1, and an observation was taken to ensure that the system was still balanced. The sector was then set running, thus reducing the effective illumination from L_1, and consequently the photoelectric current through C_1. The photoelectric current through C_2 was now decreased by the same amount by lowering the illumination from L_3 partly by closing the aperture A in the cube and partly by lowering the voltage across L_3, the latter procedure being used as a fine adjustment. When this operation was completed, the electrometer showed no deflexion. Finally, M was raised, thus illuminating C_1 by L_2, the latter being moved along the bench until the balance was restored. With this arrangement any slow changes in the response of the cell are entirely eliminated. In any set of observations it was necessary to keep constant the voltages across L_1 and L_2, and this was tested by means of a potentiometer. For this series of tests special sector disks, whose ratios were known accurately to four places of decimals, were employed.

Table VIII.—Electrometer Apparatus.

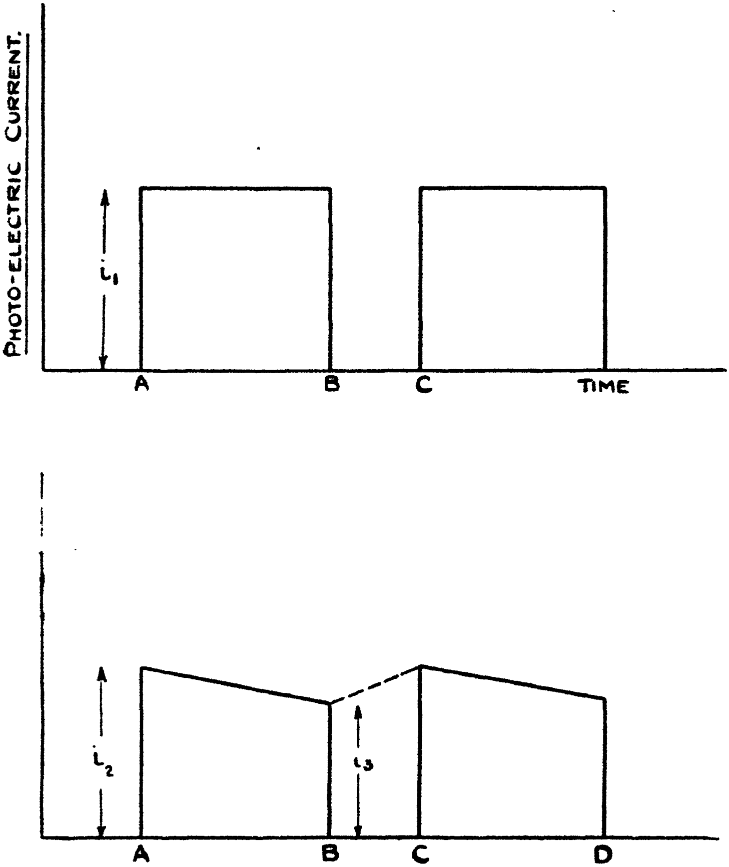
Inverse square response less sector response × 10^4. for	0·7500	0·5000	0·2500
Potassium neon cell	−14	+ 2	−12
Cæsium vacuum cell	+ 7	−10	− 4
Rubidium helium cell	−12	+ 9	+10
Rubidium vacuum cell, plate type	− 7	+ 5	0
Potassium neon cell made of uviol glass.	+ 5	+ 6	− 9

Five cells were tested on this apparatus, the results being given in Table VIII. The same photoelectric current was produced when the illumination was varied either by applying the inverse square law or by interposing a sector disk. The probable experimental error was ±0·0007.

The fact that Talbot's law holds for cells with a non-linear illumination-current relationship indicates a reason for their non-linearity. In the case of a non-linear cell, there are theoretical reasons for believing that the absence of proportionality between illumination and photoelectric current is not due to any intrinsic property of the alkali metal, but to some accidental property of the cell itself, by virtue of which the condition of the cell with regard to its internal electric fields or to gaseous layers is changed upon exposure to illumination. If we suppose this to be the case, then, if the cause of non-proportionality could be removed, the curves showing the relation between photoelectric current and illumination would become a straight line, which would be the tangent of the origin of the former non-linear curve. The tangent is shown in the lower diagram of fig. 3. It would appear then that if, in an experimental determination of the illumination-current curve of a cell, it were possible to take measurements of photoelectric current immediately after exposure to light, and between each exposure the cell could be obscured for a sufficient length of time for complete recovery from photoelectric fatigue, then the curve obtained would be linear for all cells. In practice, however, measurements can not be made instantaneously, but a lapse of several seconds must take place. With cells in which the proportionality between photoelectric current and illumination holds, the instantaneous reading and the steady reading after a few seconds are the same. For non-proportional cells, however, it would seem that a rapid fatigue occurs, which results after a few seconds in a steady reading of lower value than the instantaneous value. This assumption is supported by the fact that it furnishes an explanation why the departure from linearity of the characteristic is the same for intermittent illumination as for continuous illumination of the same average value. Considering a linear cell in the first place, and neglecting any lag due to resistance and capacity in the circuit, a sector rotating between a light and a photoelectric cell would give a time-current curve as in fig. 5 *a*. A corresponds to a point when the cell is exposed, and the photoelectric current immediately rises to i_1. At B the cell is occulted by the sector, and the current falls to zero again. At C, the cell being again exposed, the current again rises to i_1.

With a non-linear cell in which the current is less than it should be for a strict proportionality, there must be a fatigue during the time that the cell is exposed and a recovery during the time that the cell is occulted by the sector. Thus the current-time curve of such a cell intermittently illuminated after a steady state has been reached would be as shown in fig. 5 *b*. At A the cell is exposed and the photoelectric current rises to a certain value—say i_2. Between A and B the cell is exposed and the current decreases slightly, due to a rapid fatigue, to a value i_3. At B the light is cut off by the sector and the current falls to zero. While the cell is in darkness there is a tendency to recover, and the dotted line represents the potential or virtual response of the cell or the current that would flow through the cell if it were suddenly exposed at any time between B and C At C the cell is exposed by the sector, and if the steady state has been reached the current again rises to i_2. When the steady state has been reached there is a constant difference between the value of the ordinates at the beginning and end of any exposure, and the response of

Figs. 5 *a* and 5 *b*.



the cell is moving over one small portion of the fatigue curve and one small portion of the recovery curve, and these portions, if the speed of the sector is fast, are to a first approximation straight lines. The portions of the fatigue and recovery curves about which the cell oscillates are, under these conditions, independent of sector speed, being solely determined by the angular opening of the apertures.

If m_F is the slope of the portion of fatigue curve, m_R is the slope of the portion of the recovery curve, n is the number of revolutions per unit, and ω the angular opening in the sector disk, then equating the fatigue over the interval $\frac{1}{n}\frac{\omega}{2\pi}$, during which the cell is exposed to the recovery over the interval $\frac{1}{n}\left(\frac{2\pi-\omega}{2\pi}\right)$, during which the cell is occulted,

$$m_F \cdot \frac{1}{n}\frac{\omega}{2\pi} = m_R \cdot \frac{1}{n}\left(\frac{2\pi-\omega}{2\pi}\right)$$

$$\frac{m_F}{m_R} = \frac{2\pi-\omega}{\omega}.$$

Thus for a sector with angular opening ω the points of the fatigue and recovery curves about which the response of the cell will oscillate are those points where the differential coefficients are m_F and m_R respectively. Furthermore, since Talbot's law is obeyed, the portions of the fatigue and recovery curves traversed by the cell for intermittent illumination must be so situated that the combined fatigue and recovery effects lead to the same value of average photoelectric current as is obtained for the fully fatigued state of the cell in the case of continuous illumination of the same average value. This fatigue must not be confused with any slow changes in sensitivity which occur over comparatively long periods.

The non-linearity of photoelectric cells may be thus accounted for by this hypothesis of a fatigue and recovery during the periods of illumination and occultation. That this supposition is reasonable is shown by the following tests. The thermionic bridge was balanced for a given steady illumination. The galvanometer circuit was then broken, whilst the cell was covered for varying lengths of time. The cell was then exposed, and the galvanometer circuit completed after lengths of time varying from one half to five seconds. Quite distinctive galvanometer kicks were obtained after the short intervals of less than one second, and it was not until the interval reached five seconds that no deflexion was obtained. This is a point that requires further investigation.

The authors desire to express their indebtedness to Dr. J. W. J. Walsh and Professor A. O. Rankine for continued interest and advice during the work and to Mr. C. J. MacManus for extremely valuable assistance in taking observations.

XCVI. *Talbot's Law, Fatigue, and Non-Linearity in Photoelectric Cells.* By W. S. STILES, *B.Sc.* (*National Physical Laboratory*) *.

SUMMARY.

THE problem considered is that of the average response of a photoelectric cell, when illuminated with flickered light. The response of the cell is assumed to be subject to short-period fatigue and recovery. The following points are discussed: (1) the variation of average response with sector speed, (2) the relation between the existence of short-period fatigue in a cell and the obedience of the cell to Talbot's law, (3) the form of the steady response—steady illumination characteristic for a cell obeying Talbot's law.

1. *Introduction.*

IN the preceding paper Harrison and Carruthers † describe some experiments which aim at testing the applicability of Talbot's law to photoelectric cells. They find the law to hold good even in the case of certain non-linear cells, and to explain this rather unexpected result make the suggestion that the non-linearity of these cells is due to what may be termed short-period fatigue, *i. e.* fatigue which occurs in the first few seconds after switching on the light. The following analysis of the relations between Talbot's law, fatigue, and non-linearity was worked out by the writer after discussing with Harrison and Carruthers the results of their experiments. It is shown that, making the "natural" assumptions about the form of the fatigue and recovery curves, obedience to Talbot's law implies that the initial response of the cell is proportional to the light-intensity, and that in the case of non-linear cells the total amount of the fatigue is proportional to the square of the light-intensity.

2. *Average Current for a Given Light-intensity and Variable Sector Speed and Sector Angle.*

Consider a cell which has been rested for a long period in the dark. On exposing it to light-intensity I, the photo-

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* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

† "Application of Talbot's Law to Photoelectric Cells with a Non-Linear Illumination-Current Characteristic."

electric current* obtained will not in general be a constant, but will vary with time owing to fatigue effects. The current at a time τ, after switching on the light, may be represented by a function $\phi(\tau)$. $\phi(\tau)$ defines the fatigue curve of the cell. In the case of most cells, after the light has been on for some time the photoelectric current will have settled down to a steady value. The slow change in the current which occurs for exposures of an hour or more is not taken into account in the present analysis, the fatigue under consideration here being over in the first few seconds of the exposure. When the steady state has been reached, if the light be cut off, the cell will gradually recover. The course of the recovery process can be represented by the function $\chi(\tau)$, which equals the current obtained if the light is switched on after τ seconds of recovery from the fully fatigued state. It will now be assumed (*a*) that if the cell is recovering and on switching on the light the current obtained is i, then the subsequent fatigue will be represented by $\phi(\alpha+\tau)$, where α is such that $\phi(\alpha)=i$: and (*b*) that if the light is on, and the current equals i, then on switching off the light the recovery will follow the law $\chi(\beta+\tau)$, where β is such that $i=\chi(\beta)$.

When the cell is periodically illuminated to the intensity I by means of a sector disk, a steady state is arrived at finally and a certain average current is obtained. Suppose the light is exposed for an interval L and cut off for an interval D, and suppose the currents at the initial and final instants of the light period are u and v respectively. Let α and β be such that $\phi(\alpha)=u$, $\chi(\beta)=v$. It follows that

$$v=\phi(\alpha+\mathrm{L}) \quad \text{and} \quad u=\chi(\beta+\mathrm{D}).$$

Thus

$$\left.\begin{aligned}\chi(\beta)&=\phi(\alpha+\mathrm{L}),\\ \phi(\alpha)&=\chi(\beta+\mathrm{D}).\end{aligned}\right\} \quad \ldots\ldots \quad (1)$$

Given the fatigue and recovery curves, these equations suffice to determine α and β. The average current will be given by

$$\bar{i}=\frac{1}{\mathrm{L}+\mathrm{D}}\int_0^{\mathrm{L}}\phi(\alpha+t)\,dt.$$

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* In the case of a cell in which the dark current is not zero, by the photoelectric current will be meant the excess over the dark current. It will then be assumed that the dark current is independent of the state of fatigue of the cell. It is probable that the dark current in most cells is due to electrical leakage over the glass, in which case the assumption just made is certainly true.

The periods L and D can be expressed in terms of the constants ω, r, and frequency n of the sector disk. Suppose this to have r openings of angle ω radians, then

$$\mathrm{L} = \frac{1}{n}\frac{\omega}{2\pi}, \qquad \mathrm{D} = \frac{1}{n}\frac{2\pi - r\omega}{2\pi r}.$$

By adding the two equations for α and β given above, it follows that

$$\phi(\alpha) - \phi(\alpha + \mathrm{L}) = \chi(\beta + \mathrm{D}) - \chi(\beta)$$

or

$$\frac{\phi(\alpha + \mathrm{L}) - \phi(\alpha)}{\mathrm{L}} = -\frac{\mathrm{D}}{\mathrm{L}}\left\{\frac{\chi(\beta + \mathrm{D}) - \chi(\beta)}{\mathrm{D}}\right\}.$$

Thus the portions of the fatigue and recovery curves along which the cell moves are such that the average slope of the fatigue curve over the light period equals the average slope of the recovery curve over the dark period times minus the ratio of the dark to the light period. When the sector speed is sufficiently high, L and D become very small and the average slopes can be replaced by differential coefficients. In this case

$$\phi'(\alpha) = -\frac{\mathrm{D}}{\mathrm{L}}\chi'(\beta) \quad \text{and} \quad \bar{i} = \frac{\mathrm{L}}{\mathrm{L} + \mathrm{D}}\phi(\alpha) = \frac{\omega r}{2\pi}\phi(\alpha).$$

When the sector is not rotated at a very high speed, the average current will depend on the speed. Suppose for a given sector the values of α and β for infinite sector speed are α_0 and β_0, so that

$$\phi(a_0) = \chi(\beta_0) \quad \text{and} \quad \phi'(a_0) = -\frac{\mathrm{D}}{\mathrm{L}}\chi'(\beta_0).$$

For a finite sector speed put

$$\alpha = \alpha_0 + a, \qquad \beta = \beta_0 + b,$$

where a and b depend on n. Expanding the expression $\phi(\alpha + \mathrm{L})$ up to the second differential coefficient, we have approximately

$$\begin{aligned}\phi(\alpha + \mathrm{L}) &= \phi(\alpha_0 + a + \mathrm{L}) \\ &= \phi(\alpha_0) + (a + \mathrm{L})\phi'(\alpha_0) + \tfrac{1}{2}(a + \mathrm{L})^2\phi''(\alpha_0),\end{aligned}$$

and similar expressions for $\phi(\alpha)$, $\chi(\beta)$, and $\chi(\beta + \mathrm{D})$. Substituting in the equations (1) above, two simultaneous equations for a and b are obtained:

$$(a + \mathrm{L})\phi'(\alpha_0) + \tfrac{1}{2}(a + \mathrm{L})^2\phi''(\alpha_0) = b\chi'(\beta_0) + \frac{b^2}{2}\chi''(\beta_0),$$

$$a\phi'(\alpha_0) + \tfrac{1}{2}a^2\phi''(\alpha_0) = (b + \mathrm{D})\chi'(\beta_0) + \frac{(b + \mathrm{D})^2}{2}\chi''(\beta_0).$$

The approximate solution of these equations gives

$$a = -\frac{L}{2}\left\{1 - \frac{D}{4}\frac{\chi''(\beta_0)}{\phi'(\alpha_0)}\left(\frac{D}{L}\right)\right\}.$$

Now

$$\bar{i} = \frac{1}{L+D}\int_0^L \phi(\alpha+t)\,dt$$

$$= \frac{1}{L+D}\int_0^L dt\left\{\phi(\alpha_0) + (a+t)\,\phi'(\alpha_0) + \frac{(a+t)^2}{2}\,\phi''(\alpha_0)\right\}$$

On performing the integration and substituting the value of *a* found above, the average current is obtained in the form:

$$\bar{i} = \bar{i}_0\left[1 + \frac{1}{8n^2}\frac{\omega^2}{4\pi^2}\left\{\frac{1}{3} + \frac{\chi''(\beta_0)}{\phi''(\alpha_0)}\frac{D^2}{L^2}\right\}\frac{\phi''(\alpha_0)}{\phi(\alpha_0)}\right], \quad (2)$$

where $\bar{i}_0$ is the average current for infinite sector speed. It will be noticed that the effect of slowing down the sector is proportional to the square of the reciprocal of the sector frequency, and may be expected to be small. Experimentally, for sector speeds sufficiently low to detect the effect, the integrative action of the measuring system is no longer perfect, and the accuracy of the measurements falls off accordingly. It might be possible, however, to modify the apparatus to meet this difficulty; in which case the above equation would be of use in determining the shape of the fatigue and recovery curves. When certain natural assumptions are made about the fatigue effect, the result takes on a considerably more "workable" form. (See below, paragraph 4.)

3. *Talbot's Law.*

The above considerations have applied to the case of a cell exposed to a fixed illumination I flickered with a sector disk of given characteristics. For different illuminations I, the functions ϕ and χ will be different, and this may be indicated explicitly by writing $\phi(\tau, I)$ and $\chi(\tau, I)$. In what follows we are concerned solely with the average current at infinite sector speed, *i.e.*, $\frac{\omega r}{2\pi}\phi(\alpha, I)$, where α is defined by

$$\phi(\alpha, I) = \chi(\beta, I) \quad \text{and} \quad \phi_\tau'(\alpha, I) = -\frac{D}{L}\chi'(\beta, I).$$

The experiments of Harrison and Carruthers establish the validity of Talbot's law for both linear and non-linear cells.

The law takes in the present notation the following simple form:

$$\frac{\omega r}{2\pi}\phi(\alpha, \mathrm{I}) = \phi\left(\infty, \frac{\omega r}{2\pi}\mathrm{I}\right) \quad . \quad . \quad . \quad . \quad (3)$$

for any value of $\frac{\omega r}{2\pi} \leq 1$ and for all values of I.

For a linear cell,

$$\phi(\infty, \mathrm{I}) = k\mathrm{I};$$

thus

$$\frac{\omega r}{2\pi}\phi(\alpha, \mathrm{I}) = k\frac{\omega r}{2\pi}\mathrm{I}$$

or

$$\phi(\alpha, \mathrm{I}) = k\mathrm{I}.$$

It follows that

$$\phi_\tau'(\alpha, \mathrm{I})\frac{d\alpha}{d\omega r} = 0$$

and $\phi_\tau'(\alpha, \mathrm{I})$ must be zero, for otherwise $\frac{d\alpha}{d\omega r} = 0$ is inconsistent with the equations determining α. Thus the truth of the law implies in the case of a linear cell the absence of fatigue (short period). It also follows necessarily that if the cell is non-linear, fatigue must occur, for then

$$\phi(\alpha, \mathrm{I}) = \frac{\phi\left(\infty, \frac{\omega r}{2\pi}\mathrm{I}\right)}{\omega r/2\pi}$$

will vary with ωr, which can only take place through a variation of $\phi(\alpha, \mathrm{I})$ with α.

Talbot's law has enabled, therefore, a qualitative connexion to be established between fatigue and non-linearity. By making two plausible assumptions about the functions ϕ and χ, the quantitative relationship between the two effects is obtained in a very simple form.

Assumption A.

$$\phi(\tau, \mathrm{I}) + \chi(\tau, \mathrm{I}) = \phi(0, \mathrm{I}) + \phi(\infty, \mathrm{I}). \quad . \quad . \quad (4)$$

This makes the recovery process vary with the time in the same way as the fatigue process, except that it is in the opposite direction, *i. e.*,

$$\phi_\tau'(\tau, \mathrm{I}) = -\chi_\tau'(\tau, \mathrm{I}), \qquad \phi_\tau''(\tau, \mathrm{I}) = -\chi_\tau''(\tau, \mathrm{I}), \text{ etc.}$$

The equations determining α are now

$$\phi(\alpha, I) = \{\phi(0, 1) + \phi(\infty, I)\} - \phi(\beta, I)$$

and

$$\phi_\tau'(\alpha, I) = \frac{D}{L}\phi_\tau'(\beta, 1).$$

Assumption B.

$$\phi(\tau, I) = \{\phi(0, I) - \phi(\infty, I)\}e^{-\eta\tau} + \phi(\infty, I). \quad . \quad (5)$$

This says that the fatigue follows an exponential law with the time; η may vary with I. It follows from the α equations that

$$D/L = e^{-\eta(\alpha-\beta)}$$

and

$$e^{-\eta\alpha} + e^{-\eta\beta} = 1,$$

from which is obtained

$$e^{-\eta\alpha} = D/(D+L)$$

and

$$\phi(\alpha, I) = \phi(\infty, I) + \{D/(D+L)\}\{\phi(0, I) - \phi(\infty, I)\}.$$

Here

$$\phi(0, I) - \phi(\infty, I) = F(I)$$

is the total fatigue. The experimental law (3) now takes the form:

$$\sigma\phi(\infty, I) + \sigma(1-\sigma)\,F(I) = \phi(\infty, \sigma I). \quad \left[\frac{\omega\tau}{2\pi} = \sigma\right]$$

$\phi(\infty, I)$ is a function known experimentally, and hence

$$F(I) = \frac{\phi(\infty, \sigma I)}{\sigma(1-\sigma)} - \frac{\phi(\infty, I)}{1-\sigma} \quad . \quad . \quad . \quad . \quad (6)$$

is determinable The left-hand side of this equation does not contain σ. A test of the validity of assumptions A and B is afforded by seeing whether $\phi(\infty, I)$ depends on I in such a way that $\dfrac{\phi(\infty, \sigma I)}{\sigma(1-\sigma)} - \dfrac{\phi(\infty, I)}{1-\sigma}$ is invariant with respect to σ.

Suppose, further, $I' = sI (s \leq 1)$, then

$$F(I') = \frac{\phi(\infty, uI')}{u(1-u)} - \frac{\phi(\infty, I')}{1-u} = \frac{\phi(\infty, usI)}{u(1-u)} - \frac{\phi(\infty, sI)}{1-u},$$

and substituting for $\phi(\infty, usI)$ and $\phi(\infty, sI)$ the values obtained from (6) above with $\sigma = us$ and $\sigma = s$ respectively, we obtain

$$F(I') = F(sI) = s^2F(I).$$

The only function for which this is true for all values of s is $F(I)=RI^2$, where R is a constant. Thus

$$RI^2=\frac{\phi(\infty,\sigma I)}{\sigma(1-\sigma)}-\frac{\phi(\infty,I)}{1-\sigma}.$$

By differentiating partially with respect to σ and I, $\phi(\infty,\sigma I)$ and σ can be eliminated and a differential equation obtained for $\phi(\infty,I)$, which runs:

$$I\frac{d\phi}{dI}-\phi+RI^2=0.$$

The general solution of this equation is

$$\phi(\infty,I)=kI-RI^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k is a constant. This gives the final response of the cell after the first few seconds, as a function of the light-intensity. The initial response is obtained by substituting for $\{\phi(0,I)-\phi(\infty,I)\}=F(I)$ and $\phi(\infty,I)$ in equation (5), and putting τ equal to zero. We find that

$$\phi(0,I)=kI.$$

In the case of a so-called non-linear cell, therefore, obedience to Talbot's law implies that the initial response of the cell is linearly proportional to the light-intensity, but that short-period fatigue occurs which reduces the current by an amount proportional to the square of the light-intensity.

Harrison and Carruthers (*loc. cit.*) give measurements of the final response characteristics of a potassium neon-filled cell for which they also establish the applicability of Talbot's law. Their results are reproduced in columns 1 and 2 of Table I.

TABLE I.

I, arb. units.	$\phi(\infty,I)$, arb. units.	$kI-\phi(\infty,I)$.	$\frac{1}{I^2}\{kI-\phi(\infty,I)\}=R$.
1/12	·0933	(0)	—
1/8	·1377	·0023	·147
1/6	·1836	·0030	·108
1/4	·2709	·0090	·144
1/3	·3565	·0167	·150
1/2	·5232	·0366	·146
2/3	·6867	·0597	·134
3/4	·7643	·0754	·134
1	1·000	·1196	·120

According to equation (7),

$$\left.\frac{d\phi(\infty, \mathrm{I})}{d\mathrm{I}}\right|_{\mathrm{I}=0} = k,$$

and an approximate value for k is obtained, using the measured response at $\mathrm{I}=1/12$, and treating the characteristic as linear between $\mathrm{I}=0$ and $\mathrm{I}=1/12$. k then comes out to be 1·120. Columns 3 and 4 of the table give

$$k\mathrm{I}-\phi(\infty, \mathrm{I}) \quad \text{and} \quad \frac{1}{\mathrm{I}^2}\{k\mathrm{I}-\phi(\infty, \mathrm{I})\} = \mathrm{R}$$

for different values of I. The approximate constancy of the figures in the last column provides a general confirmation of the argument developed above.

4. *Further Remarks on the Average Current at Finite Sector Speeds.*

The formula (2) of paragraph 2 may be re-written

$$\bar{i} = \bar{i}_0\left[1+\frac{1}{8n^2}\frac{\sigma}{r^2}\frac{\phi''(\alpha_0)}{\bar{i}_0}\left\{\frac{1}{3}+\left(\frac{1-\sigma}{\sigma}\right)^2\frac{\chi''(\beta_0)}{\phi''(\alpha_0)}\right\}\right].$$

An experimental check of this result could be obtained by determining the variation with sector speed for two sectors having the same σ value but with different numbers of openings r. The functions $\phi''(\alpha_0)$ and $\chi''(\beta_0)$ depend only on σ, so that the coefficient of $\frac{1}{n^2}$ should vary as $\frac{1}{r^2}$.

Theoretically, if the coefficient of $\frac{1}{n^2}$ can be determined experimentally, the form of the fatigue and recovery curves can be deduced. For in that case

$$\frac{\phi''(\alpha_0)}{3}+\frac{(1-\sigma)^2}{\sigma^2}\chi''(\beta_0)$$

will be an experimentally determined function of σ, and the same is true of

$$\phi(\alpha_0) = \chi(\beta_0) = i_0/\sigma.$$

Calling these functions $g(\sigma)$ and $f(\sigma)$ respectively, and making use of the equation

$$\phi'(\alpha_0) = \frac{\sigma-1}{\sigma}\chi'(\beta_0),$$

the following differential equation is obtained for σ in terms of α_0:

$$\frac{4}{3}f'(\sigma)\frac{d^2\sigma}{d\alpha_0^2}+\left(\frac{d\sigma}{d\alpha_0}\right)^2\left\{\frac{4}{3}f''(\sigma)-\frac{1}{\sigma(\sigma-1)}f'(\sigma)\right\}=g(\sigma).$$

The solution of this equation appropriate to the boundary conditions $\sigma=0$ when $\alpha_0=0$, $\sigma=1$ when $\alpha_0=\infty$ may be written

$$\sigma = \mathrm{N}(\alpha_0),$$

and the fatigue curve is obtained immediately as

$$\phi(\alpha_0)=f(\sigma)=f\{\mathrm{N}(\alpha_0)\}.$$

The recovery curve is determinable by an analogous method.

If the two assumptions of paragraph 3 restricting the possible shape of the recovery and fatigue curves are adopted,

$$g(\sigma)=\frac{\phi''(\alpha_0)}{3}+\left(\frac{1-\sigma}{\sigma}\right)^2\chi''(\beta_0)=\eta^2\mathrm{F}(\mathrm{I})\frac{(1-\sigma)(4\sigma-3)}{3\sigma}$$

or

$$\eta^2\mathrm{F}(\mathrm{I})=\{3\sigma/(1-\sigma)(4\sigma-3)\}g(\sigma).$$

The left-hand side of the last equation does not contain σ, and the constancy of $\frac{3\sigma g(\sigma)}{(1-\sigma)(4\sigma-3)}$, determined experimentally for different values of σ would provide a further check on the assumptions A and B. No restriction has been placed on η, *i. e.*, the rapidity of the fatigue process may be different for different illuminations I. The present method enables any such variation to be detected, for $\mathrm{F}(\mathrm{I})=\mathrm{I}^2\mathrm{R}$ and $\eta^2\mathrm{F}(\mathrm{I})$ as a function of I is given by measurements of $g(\sigma)$ at different illuminations.

5. *Conclusion.*

The above considerations apply specifically to the case of photoelectric cells. It is clear, however, that the *analysis* is also valid for selenium cells * and, in fact, for all cases in which the average response to a periodically interrupted stimulus is in question. There are, however, difficulties about applying the results to human vision.

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* Further experimental work by Harrison and Carruthers indicates that in certain cases Talbot's law is also valid for selenium cells.

XCVII. *The Propagation of Sound in Gases*[*].

By D. G. Bourgin, *Ph.D., University of Illinois, U.S.A.*[†]

DURING the last few years attention has again been drawn to the propagation of sound in gases—particularly at high frequencies. The experimental work of principal consequence as regards the purposes of this paper is that of Pierce[‡] and Abello[§], and within the year there has appeared a valuable theoretical study by Herzfield and Rice[||].

An early edition of Jeans' 'Dynamical Theory of Gases' contains a treatment of the propagation of sound in a pure gas, recognizing the lag in the exchange of translational and internal energy for the case of a system of loaded spheres. Herzfeld and Rice's article deals with the extension of this hypothesis to the general case, and it is assumed that there is a uniform lag for all internal energy transfers. The present paper, begun some months before the publication of their results, makes an attempt to link up explicitly the nature of the kinetics of sound with the internal constitution of the entities composing the gas.

The first part of this work develops the ideas and equations for a theory which takes account of the collision excitation and de-excitation of the molecules composing the gas. In brief, it is assumed that under the influence of collisions of the first kind some molecules are thrown into states of higher energy from which they may return to lower energy levels either spontaneously or as the outcome of collisions of the second kind.

To fix our ideas, let us consider a gas maintained at the constant temperature T_0. The propagation of a sound-wave implies the possibility of distinguishing regions of higher and regions of less kinetic energy than the mean in the gas. For purposes of exposition we will make use of the fiction of a correlated regional translational temperature. During the perturbation of the gas we may characterize each internal state i by another fictitious temperature T_i, defined as that temperature which under equilibrium conditions associates the same number of molecules in state i.

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[*] D. G. Bourgin, 'Nature,' cxxii. p. 133 (1928).

[†] Communicated by the Author.

[‡] G. W. Pierce, Am. Acad. Sci. lx. p. 271 (1925).

[§] T. P. Abello, Proc. Nat. Acad. xiii. p. 699 (1927); Phys. Rev. Jun 1926, p. 1083.

[||] K. F. Herzfeld and F. O. Rice, Phys. Rev. xxxi. p. 691 (1928).

For low frequencies the collision mechanism is adequate to permit of exact reproduction in the internal temperatures of the pulsations in the translational temperature. At higher frequencies there is a phase-lag and then a diminution in the relative amplitudes of the several internal and the translational temperatures. These various phase-lags and the amplitude diminutions affect the absorption and decrease the effective specific heat—accordingly increasing the velocity of propagation of sound in the gas.

The Herzfeld-Rice hypothesis is also touched on as a special case of this theory, and some of the implications not hitherto exhibited are mentioned. The theory is in all respects a kinetic theory, and the agencies taken account of (exclusive of radiation) are all described in terms of their kinetic equivalents.

The second part of the paper advances a theory of sound propagation in a mixture of two gases. So far as the author is aware, this represents the first attempt to consider this problem. The theory is immediately applicable to experimental results of the type obtained by Pierce and Abello, and suggests the desirability of experimental researches to test the conclusions arrived at.

PART I.

We shall have occasion to make use of the following symbols:—

K = kinetic energy of translation of a single molecule.

δT = increment in translational temperature.

$\delta T_i = \omega_i \delta T$ = increment in internal temperature of state i.

m = mass of gas molecule.

N_i = numerical concentration of the molecules/c.c. in state i.

N = numerical gas density.

ϵ_i = energy of the level i.

$\epsilon_{ij} = \epsilon_i - \epsilon_j$.

$\nu = \bar{\nu}/2\pi$ = sound frequency.

$\bar{\lambda} = 2\pi\lambda$ = sound wave-length in gas.

u = variable molecular velocity in the x direction.

v = mass velocity in the x direction.

$V = \nu\lambda$ = velocity of sound propagation.

The essential equations may now be written :—

The equation of continuity is

$$\frac{d}{dt}\mathrm{N} = -\frac{\partial}{\partial x}\mathrm{N}v. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equation for the momentum transfer,

$$\frac{d}{dt}m\mathrm{N}v = -\frac{\partial}{\partial x}m\mathrm{N}\overline{u^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$= -\frac{2}{3m}\frac{\partial}{\partial x}\mathrm{KN}, \quad . \quad . \quad . \quad . \quad (2.1)$$

where the bar denotes a regional average.

The statement of the change in the concentration N_i,

$$\frac{d}{dt}\mathrm{N}_i = -\frac{\partial}{\partial x}\mathrm{N}_i v + \Delta\mathrm{N}_i, \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta\mathrm{N}_i$ refers to the effect of collisions. A check on equation (3) is afforded by summing over the subscript i, for, since $\Sigma\Delta\mathrm{N}_i = 0$, we obtain equation (1).

Finally, the variation in kinetic energy is expressed *,

$$\frac{d}{dt}\mathrm{NK} = -\frac{\partial}{\partial x}\frac{5}{3}v\mathrm{K} + \Delta\mathrm{K}, \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta\mathrm{K}$ represents the net contribution of the internal states or, otherwise stated, is the difference between the energy transfers arising from collisions of the first and second kinds respectively.

An expression for $\Delta\mathrm{N}_i$ more amenable to analysis is derived as follows :—

The principle of microscopic reversibility asserts that at equilibrium

$$\mathrm{N}_i^2[\bar{f}_{ij} - f_{ij}] + \mathrm{NN}_i f_{ij} - \mathrm{N}_j^2[\bar{f}_{ji} - f_{ji}] + \mathrm{NN}_j f_{ji} = 0, \quad (5)$$

where $\bar{f}_{ij}$ is the averaged probability of the transition $i \rightarrow j$ when the colliding molecules are similarly specified, and f_{ij} refers to the case that they are in different states, thus taking account of the possible coupling or resonance effect †

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* The $\frac{5}{3}$ arises from averaging $u\mathrm{K}$. *Cf.* Jeans's 'Kinetic Theory of Gases.'

† For many gases there is no appreciable coupling and the coefficients of the squared terms vanish (though there is no corresponding simplification in any of the later formulæ based on equation (5)). *Cf.*, for instance, HCl.

between molecules in similar states. The symbols $\bar{f}_{ji}$ and f_j are the probabilities for the reverse [*] encounters.

Attendant on the passage of a sound-wave the translational energy perturbations affect the probability factors f_{ij} etc., while the fluctuations in N_i are determined by the variations in the internal temperatures, i. e., $\omega_i \delta T$. Hence we may write the collision contribution to the change [†] in N^i as

$$\begin{aligned}\Delta N_i = -\sum_j \delta N[N_i f_{ij} - N_j f_{ji}] + \delta N_i[2\bar{f}_{ij} - f_{ij}]N_i + Nf_{ij} \\ -\delta N_j[(N_j(2)(\bar{f}_{ji} - f_{ji}) + Nf_{ji}] + N_i^2\delta[\bar{f}_{ij} - f_{ij}] \\ + NN_i\delta f_{ij} - \ldots \quad . \quad (5.1)\end{aligned}$$

Evidently

$$\delta N_i = \frac{\delta N}{N} N_i + \dot{N}_i \omega_i \delta K, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the symbol $\dot{N}_i$ being interpreted as $\frac{dN_i}{dK}$.

The variations in the probability factors are of the form $\frac{\partial f_{ij}}{\partial K}\delta K$. On introducing the abbreviation

$$R_{ij} = N\left[2\frac{N_i}{N}(\bar{f}_{ij} - f_{ij}) + f_{ij}\right],$$

and observing that for $\omega_i = 1$, $\Delta N_i = 0$, we write

$$\begin{aligned}\sum_j N[\delta N_i R_{ij} - \delta N_j R_{ji}] \\ = -\sum (NN_i - N_i^2)\delta f_{ij} - [N_j N - N_j^2]\delta f_{ji} + N_i^2 \delta f_{ij} - N_j^2 \delta f_{ji}. \\ . \quad . \quad . \quad (5.2)\end{aligned}$$

Substituting equation (6) in equation (5.1), and noting that the coefficient of δN becomes precisely the left side of equation (5) and is therefore 0, we have, finally,

$$\Delta N_i = -N\sum_j [\dot{N}_i R_{ij}(\omega_i - 1) - \dot{N}_j R_{ji}(\omega_j - 1)]\delta K.$$

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[*] P.A.M. Dirac, Proc. Soc. of London, cvi. A, p. 581 (1914).

[†] The matter of determining the proper sign, both here and later in equation (7), requires some care. In order to establish the negative sign above, it is observed that $N_i[\ ] - N_j[\ ]$ ($N_i[\ ]$ and $N_j[\ ]$ are no longer to be considered equilibrium values) is the difference between the number of molecules leaving the state i for the state j, and *vice versâ*. Accordingly $N_i[\ ] - N_j[\ ] > 0$ implies a diminution in N_i. Since positive ΔN_i represents an increase, the negative sign is a consequence.

The collision increment in K is equal to, and opposite in sign to, the increment in internal energy. Therefore

$$\Delta K = -\sum_i \Delta N_i \epsilon_i$$

$$= N \sum_i \sum_j (\dot N_i R_{ij}(\omega_i-1) - \dot N_j R_{ji}(\omega_j-1))\epsilon_i. \quad . \quad (7)$$

Restricting attention to sound-waves of small amplitude, we may approximate the solution for equations (1)–(4) by assuming that all the dependent variables entering our equations vary harmonically about their mean values, *i. e.*,

$$X = X_0 + \mathfrak{J}\,|\,\delta X\,|\,e^{-j(\nu t - x/\lambda)}, \quad j = \sqrt{-1}, \quad . \quad (8)$$

where $\mathfrak{J}$ refers to the imaginary part of the succeeding expression. We next remark that because of the smallness of v we may neglect products of the type $v\,|\delta X\,|$; hence the operator $\frac{d}{dt}$ may be replaced in our work by $\frac{\partial}{\partial t}$.

Our first interest is the determination of N_i. The system (3) becomes

$$j\nu\left[\frac{|\,\delta N\,|}{N} N_i + \dot N_i \omega_i\,|\,\delta K\,|\right] = j\frac{|\,\delta v\,|}{\lambda} N_i + \Delta N_i e^{-j(\nu t - x/\lambda)}. \quad (3.1)$$

Since equation (1) may be written

$$j\nu\delta N = j\frac{|\,\delta v\,|}{\lambda} N, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

we have for equation (3.1)

$$j\nu\dot N_r\omega_r\,|\,\delta K\,| = -\sum_s[\dot N_r R_{rs}(\omega_r-1) - \dot N_s R_{sr}(\omega_s-1)]\,|\,\delta K\,|. \quad . \quad . \quad . \quad (3.2)$$

Let

$$\omega_s = a_{s0} + a_{s1}\nu + a_{s2}\nu^2 + \dots \quad . \quad . \quad . \quad (9)$$

Kinetic theory assures us that for vanishing frequencies the internal and translational temperatures are equal, i. e., $a_{s0}=1$. The same conclusion may be arrived at, incidentally, on substituting equation (9) in equation (3.2) and equating to zero the coefficients of like powers of ν. For the constant term there results

$$\sum_s (a_{r0}-1)\dot N_r R_{rs} - (a_{s0}-1)\dot N_s R_{sr} = 0.$$

This is true for $r = 1, \ldots, n$; it follows* that $a_{r0} \underset{r}{\equiv} 1.$

For the coefficient of ν we get

$$j\dot{\mathrm{N}}_r a_{r0} + \mathrm{N}\sum_s \dot{\mathrm{N}}_r \mathrm{R}_{rs} a_{r1} - \dot{\mathrm{N}}_s \mathrm{R}_{sr} a_{s1} = 0, \qquad r = 1, \ldots, n. \quad (9.1)$$

Hence

$$a_{s1} = (-1)^n j \sum_{r=1}^{n} \dot{\mathrm{N}}_r \overline{\mathrm{H}}_{rs} / \mathrm{N}\Delta, \quad . \quad . \quad . \quad . \quad (10)$$

where $\overline{\mathrm{H}}_{rs}$ is the cofactor of a_r, the term in the sth column and rth row in the determinant Δ. We will show now that this is

$$a_{s1} = -j \left| \sum_{r=1}^{n} \dot{\mathrm{N}}_r \overline{\mathrm{H}}_{rs} / \mathrm{N}\Delta \right| . \quad . \quad . \quad . \quad (10.1)$$

First, we observe that all the elements of the two determinants are real. On referring back to equation (8.1), it is clear that in any given column there are one positive and $n-1$ negative elements—since the numerator determinant differs from Δ in that the sth column has been replaced by n negative terms, our result is established.

We have shown, then, that a_{s1} is negative and imaginary, so that the first effect of increasing frequency is the introduction of a *lag* into the relation between translational and internal fluctuations.

The equations obtained by equating the coefficients of higher powers of ν to 0 differ from equation (9.1) only in that a_{s1} is replaced by a_{sq}, and a_{s0} by $a_{s,q-1}$. The formal solution of these recurrence relations is

$$a_{sq} = (-j)^q \left| \frac{\sum\limits_{a_1} \ldots \sum\limits_{a_q} \dot{\mathrm{N}}_{a_1} \ldots \dot{\mathrm{N}}_{a_q} \overline{\mathrm{H}}_{a_1 s} \overline{\mathrm{H}}_{a_2 a_1} \ldots \overline{\mathrm{H}}_{a_n a_{n-1}}}{\mathrm{N}^q \Delta^q} \right|, \quad (10.2)$$

where the $\overline{\mathrm{H}}$'s retain their earlier definition. It is seen that

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[*] We have, in fact,

$$a_{r0} = \left. \begin{vmatrix} \mathrm{N}_1 \sum\limits_s \mathrm{R}_{1s} & -\mathrm{N}_2\mathrm{R}_{21} & -\mathrm{N}_3\mathrm{R}_{31} \ldots & \sum\limits_s \mathrm{N}_1\mathrm{R}_{1s} - \mathrm{N}_s\mathrm{R}_{s1} \ldots \\ -\mathrm{N}_1\mathrm{R}_{12} & & & \sum\limits_s \mathrm{N}_2\mathrm{R}_{2s} - \mathrm{N}_s\mathrm{R}_{s2} \ldots \\ -\mathrm{N}_1\mathrm{R}_{13} & & & \vdots \\ \ldots\ldots\ldots & & & \end{vmatrix} \middle/ \Delta. \right.$$

On subtracting the sum of all the other columns from the rth column in the numerator determinant, we have precisely the denominator determinant.

the a's are alternately real and pure imaginary; hence, for instance, the amplitude diminution is a second-order effect.

ω_i may be developed in descending powers of ν; but, since at the very high frequencies at which such a development would be desirable irregularities are to be expected in the behaviour of the gas, it is not thought worth while to stress this aspect of the problem. We may remark in passing, however, that a computation, the details of which are delegated to an appendix, yields the expansion

$$\omega_m = -\frac{j}{\nu}\frac{A_m \mathrm{N}}{\dot{\mathrm{N}}_m} + \frac{\mathrm{N}^2}{\nu^2}\sum_s\left(\frac{A_s \mathrm{R}_{sm}}{\dot{\mathrm{N}}_m} - \frac{A_m \mathrm{R}_{ms}}{\dot{\mathrm{N}}_m}\right), \quad . \quad (11)$$

where

$$A_m = \sum_s \dot{\mathrm{N}}_m \mathrm{R}_{ms} - \dot{\mathrm{N}}_s \mathrm{R}_{sm}.$$

It may be easily verified that the expression for $\Delta\mathrm{K}$ can be written

$$\Delta\mathrm{K} = \mathrm{N}\sum_r\sum_s(\dot{\mathrm{N}}_r \mathrm{R}_{rs} a_{rq} \epsilon_{rs})\,\nu^q.$$

On taking account of equation (7.1), we may write equation (4) in the form

$$j\nu\{|\delta\mathrm{N}|\,\mathrm{K} + \mathrm{N}\,|\delta\mathrm{K}|\} = \left(\frac{5}{3}\right)\frac{\mathrm{N}\mathrm{K}\,|\delta v|}{\lambda} + \sum_r\sum_s \mathrm{N}\nu^q a_{rq}\dot{\mathrm{N}}_r \mathrm{R}_{rs}\epsilon_{rs}. \quad . \quad . \quad . \quad (4.1)$$

Equation (2.1) may be expressed

$$\mathrm{N}\nu\,|\delta v| = \frac{2}{3\lambda m}(\mathrm{N}\,|\delta\mathrm{K}| + |\delta\mathrm{N}|\,\mathrm{K}). \quad . \quad . \quad (2.2)$$

On eliminating the moduli of the harmonic terms, there results

$$j\left[\begin{matrix}3m\mathrm{V}^2 - \frac{10}{3}\mathrm{K}\\ 3m\mathrm{V}^2 - 2\mathrm{K}\end{matrix}\right] = \sum_s\sum_r a_{sr}\nu^{r-1}\mathrm{B}_s, \quad . \quad (12)$$

where

$$\mathrm{B}_s = \sum_r \dot{\mathrm{N}}_r \mathrm{R}_{sr}\epsilon_{sr}.$$

Recalling (equation (10.2)) that $a_{sr} = \frac{(-j)^r}{\mathrm{N}^r}b_{sr}$, b_{sr} real, we derive

$$\frac{1}{\mathrm{V}^2} = \frac{3m}{\mathrm{K}}\left[\frac{\mathrm{N} + (\sum_s\sum_r b_{sr}\nu^{r-1}\mathrm{B}_s/\mathrm{N}^{r-1})}{\frac{10}{3}\mathrm{N} + 2\sum_s\sum_r b_{sr}\nu^{r-1}\mathrm{B}_s/\mathrm{N}^{r-1}}\right]. \quad . \quad (12.1)$$

For low frequencies this reduces to

$$\frac{1}{\mathrm{V}_0^2} = \frac{3m}{\mathrm{K}}\left[\frac{\mathrm{N} + b_1\mathrm{B}}{\frac{10}{3}\mathrm{N} + 2b_1\mathrm{B}}\right], \quad . \quad . \quad . \quad . \quad (13)$$

where $$b_r = \sum_s b_{sr}B_s / \sum_s B_s = \sum_s b_{sr}B_s/B,$$

$3kB\,\delta T/2N$=change of energy/unit time/collision for a uniform temperature difference of δT between the translational and internal temperatures.

The Laplace formula for sound velocity may be written

$$\frac{1}{V_0^2} = \frac{3m}{K}\left[\frac{3+2\beta}{10+4\beta}\right], \quad . \quad . \quad . \quad . \quad (14)$$

where β stands for the number of internal degrees of freedom.

If we equate the values for V_0^2 given by equations (13) and (14), there results, after a little algebra,

$$\begin{aligned} b_1 &= 2\beta N/3B \\ &= \beta Nk/B(dT/dK). \quad . \quad . \quad . \quad . \quad (15) \end{aligned}$$

This relation [*] defines the mean time-lag in terms of the other constants of the gas, and is expected to hold exactly if β is determined from low-frequency data. At high frequencies the measured specific heat is different, and we may, in fact, write

$$\beta = \sum_{r=0}^{\infty} \beta_r \nu^r.$$

Equation (15) involves β_0.

The mean phase-lag in seconds is then $4\pi\beta/3B$ seconds, or about $4\pi\beta\bar{\nu}/3B$ cycles. Assuming the plausible [†] value $B \sim 10^{-8}$, it seems that the average lag of internal fluctuation behind changes in translational motion is about 10^{-7} second.

The absorption depends on the imaginary terms in the expansion of $\frac{1}{V}$ —to a first approximation :

$$\frac{1}{V^2} = \frac{1}{V_0^2}\left[1 - \frac{6j\nu \sum_s b_{s2}B_{s2}}{N^2(5+2\beta)(3+2\beta)}\right]; \quad . \quad . \quad (16)$$

$$\therefore \quad \frac{1}{V} = \frac{1}{V_0}\left[1 - \frac{3j\nu b_2 B}{N^2(5+2\beta)(3+2\beta)}\right]. \quad . \quad . \quad (16.1)$$

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[*] A somewhat more direct method of deriving equation (15), though not the most obvious, for a first attempt is based on the fact that

$$\begin{aligned} \frac{d}{dt}\Sigma N_r \epsilon_r &= j\nu b_1 B \exp j(\nu t - x/\lambda) \\ &= j\nu\beta N \frac{d\,\delta K}{dt}. \end{aligned}$$

[†] Based on the data given in Herzfeld & Rice's paper.

Similarly, taking account of the real terms, it is possible to find the amplitude diminution in response of internal temperature; we shall not, however, concern ourselves here with this continuation except to observe that this term would, of course, involve b_3 (and b_2).

Entirely analogously to the expansions at low frequencies we may develop asymptotic formulæ useful at super frequencies. We have, in fact,

$$\begin{aligned}\frac{1}{V^2} &= \frac{9m}{10K}[1+2jB/5\nu \ldots] \\ &= \frac{1}{V_\infty^{\,2}}[1+2jB/5\nu \ldots]. \quad . \quad . \quad . \quad (17)\end{aligned}$$

V_∞ is the velocity for a gas with no internal degrees of freedom, and B has already been defined *.

Heretofore we have considered, in the interest of simplicity, merely the influence of collisions of the first and second kinds on the propagation of sound. Another agency in modifying our velocity and absorption is that of radiation. We may take account of this by redefining our R_{rs} and R_{sr} to be

$$\begin{aligned}N\bar{R}_{rs} &= NR_{rs}+\rho(\bar{\nu}_{rs})B_{rs} \qquad \epsilon_s>\epsilon_r \\ &= NR_{rs}+A_{rs} \qquad\qquad \epsilon_s<\epsilon_r, \quad . \quad (18)\dagger\end{aligned}$$

where $\rho(\bar{\nu}_{rs})$ is the density of black-body radiation of frequency ν_{rs} at the temperature T_0; B_{rs}, and A_{rs} are the well-known Einstein coefficients.

At ordinary temperatures the state $s(\neq 0)$ is usually one above the mean energy level; it is therefore an unstable state, and it seems likely that most collisions will result in transitions to lower energy levels. Certainly the permitted transitions for radiation changes are at least as likely as other collision transitions and, since the number of states

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* A more complete expansion is derivable from equation (11); for terms only as far as $\frac{1}{\nu^2}$ we should use

$$\frac{1}{V^2} = \frac{3m}{K}\left[\frac{1+\frac{jB}{\nu}-\sum\limits_s \frac{NA_sB_s}{\dot{N}_s\nu^2}}{\frac{10}{3}+2\left[j\frac{B}{\nu}-\sum\limits_s \frac{NA_sB_s}{\dot{N}_s\nu^2}\right]}\right].$$

† At very high temperatures we must, of course, write for the case $\epsilon_r>\epsilon_s$,

$$N\bar{R}_{rs} = NR_{rs}+A_{rs}\left(1+\rho(\bar{\nu}_{rs})\frac{8\pi h\bar{\nu}_{rs}^{\,3}}{C^3}\right).$$

which contribute appreciably to the specific heat at ordinary temperatures is not very large, NR_{sr} is of the order of magnitude of the collision frequency to within a probable factor of 10^{-2} or so. At N.T.P, therefore, NR_{sr} would be 10^8 or greater.

Since for low temperatures

$$\begin{aligned} N_r B_{rs} \rho(\nu_{rs}) &\sim A_{sr} N_s, \\ N_r R_{rs} &\sim R_{sr} N_s, \end{aligned}$$

it follows that the relative importance of the types of changes out of state r, e.g. $(B_{rs}\rho(\bar{\nu}_{rs}) : NR_{rs})$ is the same as that of changes to the state r, e.g. $(A_{sr} : NR_{sr})$. The values of A_{sr}, for the states contributing appreciably to the specific heat, for many molecules (for instance, HCl) is of the order of 10^{-2}, so that the radiation terms may usually be neglected. At high temperatures or low densities the radiation effect becomes of increasing relative importance.

As regards viscosity, it is to be noticed that the term involving it would enter only in equation (4), and, to the approximation we are making, it would appear additively in the expression for the absorption coefficient. Its value, as given by Lord Rayleigh [*], is $2\tau\nu^2/3mNV^3$, where τ is the coefficient of viscosity. Since the exponent for diminution of intensity is twice that for amplitude change, there results for the total fractional intensity change in a sound-wave after travelling the distance x,

$$\exp - \frac{8\pi^2\nu^2 x}{\bar{V}} [3\{b_2 B/N^2(5+2\beta)(3+2\beta)\} + \{\tau/3mNV^2\}]. \quad . \quad . \quad . \quad (19)$$

Further detailed progress in the general theory depends on a knowledge of the R_{rs} probabilities [†]. Let us consider now the Herzfeld-Rice assumption of a single internal temperature. This amounts in our work to writing

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[*] Rayleigh, 'Theory of Sound,' ii. par. 346.

[†] To indicate the nature of the difficulties in determining R_{rs} more clearly, we consider the correspondence principle aspect of the problem. If the electric moment of the molecule be expanded in inverse powers of ν, we may consider the various terms as being the contributions of a dipole, a superposed quadrupole, etc. For the case of radiation transition probabilities (the Einstein co-efficients) for, say, polar molecules only the 1st term's contribution is relatively important. In the case of the collision transition probabilities, the higher moments are almost of the same interest as the dipole contribution. Of course it is possible to work out our theory for an idealized case in which the higher moments are all 0—here the collision transition probabilities would be simply connected with the Einstein coefficients, but the results to be expected will hardly be of general application. *Cf.* in this connexion Nordheim, *Zeit. f. Physik*, xxxvi. p. 496 (1926).

$$\omega_r \underset{r}{\equiv} \omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

It will be seen that this implies that equation (10.2) may be written

$$\begin{aligned} a_{sq} \underset{s}{\equiv} a_q &= [-j\sum_{a_1} \dot{N}_{a_1}\overline{H}_{a_1 s}/N\Delta]^q \\ &= a^q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20.1) \end{aligned}$$

Hence, assuming the validity of equation (15), it would follow that

$$\omega = 1 - \frac{2}{3}j\nu\frac{\beta}{B} - \frac{4}{9}\frac{\beta^2}{B^2}\nu^2 + \dots \quad . \quad . \quad . \qquad (21)$$

The asymptotic expansion is here †

$$\omega = -jb_1 + \frac{b_1^2}{\nu^2}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

It will be observed that the parameters in the expansions at super frequencies (*i. e.*, equation (11), note *, p. 829, equation (22)) are those involved in the expressions we have obtained for long wave-lengths.

It is important to remark that the extreme assumption $\omega_r \underset{r}{\equiv} \omega$ is unnecessary if the velocity for small frequencies be the question of interest, for in either case we have just one unknown parameter; but it does relate b_r $(r > 1)$ to b_1, and hence leads to more definite formulæ when higher-order effects, such as absorption or amplitude diminution of internal fluctuations, are investigated. It is clear, of course, that equation (20) can be only a rough sort of approxima-

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† The same expansions are also easily derived from the fact that for ω_r independent of r

$$\begin{aligned} \omega_r &= \frac{NA_r}{j\nu\dot{N}_r + NA_r} \\ &= 1 - j\nu\frac{\dot{N}_r}{NA_r} - \nu^2\left(\frac{\dot{N}_r}{NA_r}\right)^2 + \dots, \end{aligned}$$

and also

$$= -\frac{j}{\nu}\frac{NA_r}{\dot{N}_r} + \frac{1}{\nu^2}\left(\frac{NA_r}{\dot{N}_r}\right)^2;$$

the coefficient of the term in $-j\nu$ is our previously-defined b_1, i. e.

$$b_1 = \frac{\dot{N}_r}{A_r}, \quad \text{etc.}$$

tion to the truth, whose accuracy probably diminishes with increasing q, so that the predictions are those of order of magnitude only.

The diminution in amplitude of internal variations as compared with the changes in translational energy is of the order of

$$1-2\left(\frac{b_1}{N}\right)\nu^2+\left(\frac{b_2}{N}\right)^2:1$$

or

$$1-\frac{4\pi^2}{9}\left(\frac{\beta\nu}{B}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Even for frequencies of 10^5 the diminution is expected to be negligible—accordingly the principal effect is the phase-lag. We may write equation (19) now as

$$\exp-\frac{8\pi^2\nu^2 x}{V}\left[\frac{4}{3}\frac{\beta^2}{B(5+2\beta)(3+2\beta)}+\frac{\tau}{3mNV^2}\right] . \quad (19{\cdot}1)$$

PART II.

The general problem of the propagation of sound-waves in mixed gases does not seem to have been treated previously. It is possible to extend our general theory involving different values of ω_r in a formal way—just as in the case of the pure gas it is feasible to obtain an expression for the velocity of propagation at low frequencies in terms of the mean phase displacement determined by relations analogous to equation (15) without further *ad hoc* assumptions; however, in order to exhibit the absorption we shall be forced to make simplifying hypotheses. For this reason we shall carry through the whole development on the basis of our restrictive hypotheses, bearing in mind the more general validity of our velocity formula.

Assume that in a mixture of gases A and B, the internal temperature variations of the two types of molecules are independent of the state considered, and may be characterized by the symbols $\omega_A\delta T$ for the molecules A, and $\omega_B\delta T$ for the B molecules. We shall use m_A and m_B to denote the respective masses, and N_A and $N-N_A=N_B$ for the concentrations.

Applying the equation of continuity to each of the components, we have

$$\nu\,|\,\delta N_A\,| = N_A\,|\,\delta v\,|/\lambda,$$
$$\nu\,|\,\delta(N-N_A)\,| = (N-N_A)\,|\,\delta v\,|/\lambda. \quad . \quad . \quad (24)$$

To find the analogue of equation (1) we observe, first, that the mass motion must be the same for the molecules of each gas, and, secondly, that the $\overline{u^2}$ occurring in equation (2) is to be replaced by $[\mathrm{N_A}\overline{u_\mathrm{A}^2}+(\mathrm{N}-\mathrm{N_A})\overline{u_\mathrm{B}^2}]/\mathrm{N}$. Accordingly,

$$\frac{d}{dt}\mathrm{N}v=-\frac{\partial}{\partial x}\left[\frac{2}{3m_\mathrm{A}}\mathrm{N_A K_A}+\frac{2}{3m_\mathrm{B}}(\mathrm{N}-\mathrm{N_A})\mathrm{K_B}\right]. \quad (25)$$

There is no collision term here because the condition for its appearance is a difference in mass motion.

The equipartition theorem asserts that

$$\mathrm{K_A}=\mathrm{K_B}=\mathrm{K}.$$

Therefore

$$\mathrm{N}\nu\,|\delta v|-\left[\frac{2}{3\lambda}\left\{\frac{1}{m_\mathrm{A}}(|\delta\mathrm{N_A}|\,\mathrm{K}+\mathrm{N_A}\,|\delta\mathrm{K}|)\right.\right.$$
$$\left.\left.+\frac{1}{m_\mathrm{B}}(|\delta(\mathrm{N}-\mathrm{N_A})|\,\mathrm{K}+(\mathrm{N}-\mathrm{N_A})\,|\delta\mathrm{K}|)\right\}\right]. \quad (25.1)$$

On solving equation (25.1) simultaneously with equation (24)

$$\left.\begin{aligned}|\delta v|&=\frac{2\mathrm{VS}\,|\delta\mathrm{K}|}{3\mathrm{NV^2}-2\mathrm{SK}},\\ |\delta\mathrm{N}|&=\frac{2\mathrm{N}\lambda^2\mathrm{S}\,|\delta\mathrm{K}|}{3\mathrm{NV^2}-2\mathrm{SK}},\end{aligned}\right\}\quad .\ .\ .\ .\ .\ (26)$$

where $$\mathrm{S}=\frac{\mathrm{N_A}}{m_\mathrm{A}}+\frac{\mathrm{N}-\mathrm{N_A}}{m_\mathrm{B}}=\mathrm{N}\overline{m^{-1}}.$$

We shall use the symbols R_{rs}, P_{rs} for the transition probabilities associated with collisions of two A or two B molecules, and the same symbols capped with a bar to denote the correlated quantities in an AB-type collision. With this understanding,

$$\Delta\mathrm{K}=|\delta\mathrm{K}|\,[(\omega_\mathrm{A}-1)\{\mathrm{N_A}\sum_r\sum_s\mathrm{N_A}\dot{\mathrm{N}}_{\mathrm{A}r}\mathrm{R}_{rs}\epsilon_{rs}+(\mathrm{N}-\mathrm{N_A})\overline{\mathrm{R}}_{rs}\epsilon_{rs}\dot{\mathrm{N}}_{\mathrm{A}r}$$
$$+(\omega_\mathrm{B}-1)\{\sum_p\sum_q(\mathrm{N}-\mathrm{N_A})\,(\overline{\mathrm{N}\dot{-}\mathrm{N_A}})_p\mathrm{P}_{pq}\epsilon_{pq}$$
$$+\mathrm{N_A}(\overline{\mathrm{N}\dot{-}\mathrm{N_A}})_p\overline{\mathrm{P}}_{pq}\epsilon_{pq}. \quad (27)$$

We introduce

$$\left.\begin{aligned}\mathrm{L}_1&=\sum_r\sum_s\dot{\mathrm{N}}_{\mathrm{A}r}\mathrm{R}_{rs}\epsilon_{rs}/\mathrm{N_A},\\ \overline{\mathrm{L}}_1&=\sum_r\sum_s\dot{\mathrm{N}}_{\mathrm{A}r}\overline{\mathrm{R}}_{rs}\epsilon_{rs}/\mathrm{N_A},\\ \mathrm{L}_2&=\sum_p\sum_q(\overline{\mathrm{N}\dot{-}\mathrm{N_A}})_p\mathrm{P}_{pq}\epsilon_{pq}/\mathrm{N}-\mathrm{N_A},\\ \overline{\mathrm{L}}_2&=\sum_p\sum_q(\overline{\mathrm{N}\dot{-}\mathrm{N_A}})_p\overline{\mathrm{P}}_{pq}\epsilon_{pq}/\mathrm{N}-\mathrm{N_A}.\end{aligned}\right\}\quad .\ .\ (28)$$

Then

$$\begin{aligned}\Delta K = |\delta K| \, [\omega_A[N_A^2 L_1 + (N-N_A)N_A\overline{L}_1] \\ +\omega_B[(N-N_A)^2 L_2 + N_A[N-N_A]\overline{L}_2] \\ -N_A^2[(L_1+L_2)-(\overline{L}_1+\overline{L}_2)] \\ -NN_A[L_1+\overline{L}_2-2L_2]-N^2L_2 \quad . \quad (27.1) \\ = |\delta K| (\omega_A\Phi_2+\omega_B\Phi_3-\Phi_1). \quad (27.2)\end{aligned}$$

The relation

$$\Phi_1 = \Phi_2 + \Phi_3 \quad . \quad . \quad . \quad (27.3)$$

will frequently be made use of.

The equation for the variation in N_A becomes

$$\omega_A \underset{r}{\equiv} \frac{1}{j\nu\left(\dfrac{\dot{N}_{Ar}}{\dot{N}_{Ar}(N_A R_{rs} + (N-N_A)\overline{R}_{rs} - \dot{N}_{As}(N_A R_{sr} + (N-N_A)\overline{R}_{sr})}\right)+1} . \quad (28)$$

ω_B is given by a similar equation.

The constants c_1, c_2, d_1, d_2 are defined as

$$c_1 = \left(R_{rs} - \frac{\dot{N}_{As}}{\dot{N}_{Ar}} R_{sr}\right),$$

$$c_2 = \left(\overline{R}_{rs} - \frac{\dot{N}_{As}}{\dot{N}_{Ar}} \overline{R}_{sr}\right),$$

$$d_1 = \left(P_{pq} - \frac{\dot{\overline{(N-N_A)}}_q}{\dot{\overline{(N-N_A)}}_p} P_{qp}\right),$$

$$d_2 = \left(\overline{P}_{pq} - \frac{\dot{\overline{(N-N_A)}}_q}{\dot{\overline{(N-N_A)}}_p} \overline{P}_{qp}\right).$$

Then

$$\omega_A = \frac{1}{j\nu\left[\dfrac{1}{c_1 N_A + c_2(N-N_A)}\right]+1} = \frac{1}{j\nu\vartheta_2+1}, \quad (28.1)$$

$$\omega_B = \frac{1}{j\nu\left[\dfrac{1}{d_1(N-N_A) + d_2 N_A}\right]+1} = \frac{1}{j\nu\vartheta_3+1}. \quad (28.2)$$

It is to be noticed that c_1 is a characteristic constant for the pure gas A, and is, in fact, precisely N/b_{A1}. Hence

$$c_1 = \frac{L_1}{\beta_A k}\frac{dK}{dT} \quad . \quad . \quad . \quad (29)$$

Also

$$d_1 = \frac{L_2}{\beta_B k}\frac{dK}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.1)$$

The assumptions of independence as regards r, of ω_A and c_1 (and ω_B and d_1), imply the constancy of c_2 (and d_2). We may, however, go further, *i. e.*,

$$c_2 \underset{r}{\equiv} \frac{(\dot{N}_{Ar}\overline{R}_{rs} - \dot{N}_{As}\overline{R}_{sr})\epsilon_r}{\dot{N}_{Ar}\epsilon_r}.$$

By composition we have, therefore,

$$c_2 = \frac{\sum\limits_r \sum\limits_s (\dot{N}_{Ar}\overline{R}_{rs} - \dot{N}_{As}\overline{R}_{sr})\epsilon_r}{\sum\limits_r \dot{N}_{Ar}\epsilon_r}$$

$$= \frac{\sum\limits_r \sum\limits_s \dot{N}_{Ar}\overline{R}_{rs}\epsilon_{rs}}{\frac{d}{dK}\Sigma N_{Ar}\epsilon_r}$$

$$= \frac{\overline{L}_1 \frac{dK}{dT}}{\beta_A k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.2)$$

Similarly,

$$d_2 = \frac{\overline{L}_2 \frac{dK}{dT}}{\beta_B k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.3)$$

Except for the more involved expansion for ΔK, the energy transfer equation is the same as in Part I. With the aid of equations (26) it may be exhibited in the form :

$$j\nu N\left[\frac{3NV^2 - \frac{10}{3}SK}{3NV^2 - 2SK}\right] - \frac{\Phi_2}{j\nu\vartheta_2 + 1} - \frac{\Phi_3}{j\nu\vartheta_3 + 1} + \Phi_2 = 0. \quad (30)$$

On solving for $\frac{1}{V^2}$, the term independent of ν is seen to contain $\Phi_2 + \Phi_3 - \Phi_1$, and is therefore 0. To a first approximation we have, bearing in mind equation (27.3),

$$\frac{1}{V_0^2} = \frac{3N}{KS}\,\frac{N + (\vartheta_2\Phi_2 + \vartheta_3\Phi_3)}{\frac{10}{3}N + 2(\vartheta_2\Phi_2 + \vartheta_3\Phi_3)}. \quad . \quad . \quad (31)$$

Expanded, this is

$$\frac{1}{V_0^{\,2}} =$$

$$\frac{3N}{KS}\,\frac{\left[a\left(\frac{N_A}{N}\right)^3+(b+c)\left(\frac{N_A}{N}\right)^2+(d+e)\left(\frac{N_A}{N}\right)+(\bar{\beta}_B+1)L_2\bar{L}_1\right]}{2a\left(\frac{N_A}{N}\right)^3+\left(2b+\frac{10}{3}c\right)\left(\frac{N_A}{N}\right)^2+\left(2d+\frac{10}{3}e\right)\frac{N_A}{N} + \left(2\bar{\beta}_B+\frac{10}{3}\right)L_2\bar{L}_1}, \quad . \quad . \quad . \quad (31.1)$$

where

$$\bar{\beta} = \tfrac{2}{3}\beta$$

and

$$a = (L_1-\bar{L}_1)(\bar{L}_2-L_2)(\bar{\beta}_A-\bar{\beta}_B),$$

$$b = [L_2(L_1-\bar{L}_1)+\bar{L}_1(\bar{L}_2-L_2)]\bar{\beta}_A + [2L_2(\bar{L}_1-L_1)+\bar{L}_2(L_1-\bar{L}_1)+\bar{L}_1(L_2-\bar{L}_2)]\bar{\beta}_B,$$

$$c = (L_1-\bar{L}_1)(\bar{L}_2-L_2),$$

$$d = \bar{L}_1L_2\bar{\beta}_A+(L_2(L_1-3\bar{L}_1)+\bar{L}_2\bar{L}_1)\bar{\beta}_B,$$

$$e = L_2(L_1-\bar{L}_1)+\bar{L}_1(\bar{L}_2-L_2).$$

Two intermediate checks on the accuracy of the general expression for $\frac{1}{V_0^{\,2}}$ are obtained from the two limiting values for $N_A \rightarrow 0$ or $N_A \rightarrow N$. It is readily verified that these limiting values of equation (31.1) are precisely the La Place expressions for the velocity in gas A or B respectively.

We may point out here that in order to obtain the expansion for $\frac{1}{V_0^{\,2}}$ $\left(\text{and, in fact, for } \frac{1}{V^2}\right)$ in terms of $\frac{N_B}{N}$, it is only necessary to write N_B instead of N_A, and the subscript j for i, where $\left\{\begin{matrix} i \\ j \end{matrix}\right. = 1, 2$ in equation (31.1)—hence entirely analogous simplifications in equation (31.1) may be made for very high or very low N_A concentrations.

We may remark the notable simplification of our formula for molecules with no internal degrees of freedom (or at very low temperatures) for the velocity is then given by

$$\frac{1}{V_0}=\sqrt{\frac{3N}{KS}},$$

which seems quite plausible.

In theory all four parameters L_1, $\bar{L}_1$, L_2, $\bar{L}_2$ are obtainable from experimental data on the velocity variation with concentration. Of these, L_1 and L_2 are also involved separately in the two absorption coefficients for the pure gases. Equation (31.1) is, of course, rather unwieldy (even in the case $\beta_A=\beta_B$, for which the terms in the cubes of the concentrations drop out). The experimenter desiring to test the foregoing formulæ will see how to make the obvious simplifications at low and high concentrations (a real general simplification would depend on a closer study of the L's). We can say here, as regards their order of magnitude, that a rough estimate would be $\frac{10^{-7}}{N}$ for strong to about $\frac{10^{-9}}{N}$ for weak absorption.

In order to determine the absorption in the general case, it is necessary to write down the complete expression for $\frac{1}{V^2}$. Reference to equation (30) yields

$$\frac{1}{V^2}=\frac{3N}{KS}\,\frac{\left[N+(\vartheta_2\phi_2+\vartheta_3\phi_3)+j\nu\left[(\vartheta_2+\vartheta_3)N+\phi_1\vartheta_2\vartheta_3\right]-\nu^2\vartheta_2\vartheta_3N\right.}{\frac{10}{3}N+2(\vartheta_2\phi_2+\vartheta_3\phi_3)+\nu\left[\frac{10}{3}(\vartheta_2+\vartheta_3)N+2\phi_1\vartheta_2\vartheta_3\right]-\frac{10}{3}N\nu^2\vartheta_2\vartheta_3}, \quad . \; . \; . \quad (32)$$

or

$$\frac{1}{V}=\frac{1}{V_0}\left[1-\frac{j\nu N(\vartheta_3{}^2\phi_3+\vartheta_2{}^2\phi_2)}{5N^2+8N(\vartheta_3\phi_3+\vartheta_2\phi_2)+3(\vartheta_2\phi_2+\vartheta_3\phi_3)}+\dots,\right. \quad . \; . \; . \quad (33)$$

where it is to be noticed that V_0, also, involves N_A. The expanded form for the imaginary part[*] of $\frac{1}{V}$ evidently reduces to the quotient of a 4th-degree by a 6th degree polynomial in N_A. The complete expansion may be supplied by the reader. If we confine ourselves to very small N_A concentrations (a similar expansion is true for N_A large, *cf. supra*) and retain terms up to the 2nd degree only, we have for the numerator

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[*] We may, of course, easily calculate the value of the diminution in amplitude, but the result is hardly verifiable.

$$\frac{N_A^2}{N^2}\{[L_2^2[L_1-\bar{L}_1]+2L_1[\bar{L}_2-L_2]L_2]\bar{\beta}_A^2$$
$$+[(L_2-\bar{L}_2)\bar{L}_1^2+2(\bar{L}^2-2L_2)(L_1-\bar{L}_1)\bar{L}_1$$
$$+L_2(L_1-\bar{L}_1)^2]\bar{\beta}_B^2\}$$
$$+\frac{N_A}{N}\{[L_2^2\bar{L}_1\bar{\beta}_A^2+[(\bar{L}_2-2L_2)\bar{L}_1^2+2L_2(L_1-\bar{L}_1)\bar{L}_1]\bar{\beta}_B^2$$
$$+\bar{\beta}_B^2L_2\bar{L}_1^2\}.$$

The denominator is the product of the numerator and denominators of the fraction in equation (31.1), exclusive of the factor $\frac{3N}{KS}$.

It may be pointed out that the assumption $L_i=L_i$ would be tantamount to considering the mixture to be a single gas for which the parameters $\frac{\beta^2}{L}$ and β were the means of the values for the components.

Abello* measured the ratio of the absorption in air to that of air mixed with another gas. On our theory it is clear that the ratio of the transmitted intensities is e raised to the quotient of two 6th-degree polynomials† in the concentrations‡. For the special case that $L_i=\bar{L}_i$ we write the ratio of the transmissions as

$$\frac{I_{\text{mixture}}}{I_{\text{air}}}=\exp-\frac{8\pi^2\nu^2x\left[g_1\left(\frac{N_A}{N}\right)^2+g_2\left(\frac{N_A}{N}\right)+g_3\right]}{\left\{g_4\left(\frac{N_A}{N}\right)^2+g_5\left(\frac{N_A}{N}\right)+g_6\right\}NV_mV_A},$$

where the subscript A refers to air, and

$$g_1=-\frac{16}{27}\frac{\beta_B^2}{L_2}(\beta_A-\beta_B)^2,$$

$$g_2=\frac{4}{3}\left\{\frac{\beta_A^2}{L_1}\bar{H}V-\frac{\beta_B^2}{L_2}\left(\bar{H}V\right.\right.$$
$$\left.\left.+\left[\frac{16}{3}(\beta_A-\beta_B)+\frac{8\beta_B}{3}(\beta_A-\beta_B)\right]V_m\right)\right\},$$

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* T. P. Abello, Proc. Nat. Acad. xiii. p. 699 (1927); Phys. Rev. June 1926, p. 1083.

† Assuming for the moment that air is a single gas.

‡ Exclusive of the dependence of S on N_A.

$$g_3 = \frac{4}{9}\mathrm{H}\frac{\beta_B{}^2}{L_2}(V - V_m),$$

$$g_4 = \frac{4}{3}(\beta_A - \beta_B)^2,$$

$$g_5 = \frac{16}{3}(\beta_A - \beta_B) + \frac{8}{3}\beta_B(\beta_A - \beta_B),$$

$$g_6 = \bar{\mathrm{H}} = \left(5 + \frac{16}{3}\beta_B + \frac{4}{3}\beta_B{}^2\right),$$

V = sound velocity in air,

V_m = sound velocity in the mixture.

For the case $\beta_A = \beta_B$ this reduces still further; thus

$$\frac{I_{\text{mixture}}}{I_{\text{air}}} = \exp - \frac{8\pi^2\nu^2\left[\frac{4}{3}V\left(\frac{\beta_A{}^2}{L_1} - \frac{\beta_B{}^2}{L_2}\right)\frac{N_A}{N} + \frac{4}{9}\frac{\beta_B{}^2}{L^2}(V - V_m)\right]}{N V_m V}.$$

Abello's empirical conclusion was that the logarithm of the ratio of the transmissions is a linear function of the concentration. It does not seem from our results that this can be true in general; and, even in the most favourable case, namely that in which the gases dealt with are properly characterized by the assumption $L_i = \bar{L}_i$, we should expect ordinarily the ratio of two quadratics in the concentrations *. Abello's relation holds in this extreme case only when the number of degrees of freedom of the component gases are the same and $\frac{1}{m_A}$ is not very different from $\frac{1}{m_B}$.

A number of topics for experimental study are suggested by the foregoing analysis, the details of which may be easily extended to the general case of mixtures of n gases.

APPENDIX.

To derive equation (11) we proceed as follows:—
Equation (3.2) may be written in the form

$$\omega_r - \lambda N \Sigma\left(R_{rs}\omega_r - \frac{\dot{N}_s}{\dot{N}_r}R_{sr}\omega_s\right) = -\lambda N \frac{A_r}{\dot{N}_r},$$

where $\lambda = \frac{j}{\nu}$.

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* Exclusive of the dependence of S on N_A.

On solving for ω_m, the denominator determinant is seen to be of the form

$$\begin{vmatrix} 1-\lambda N\sum\limits_s R_{1s} & \lambda\dfrac{\dot{N}_2}{\dot{N}_1}R_{21} \ldots & \lambda\dfrac{\dot{N}_n}{\dot{N}_1}R_{n1} \\ \lambda\dfrac{\dot{N}_1}{\dot{N}_n}R_{1n} & & 1-\lambda N\sum\limits_s R_{ns} \end{vmatrix} = \Delta.$$

On expanding the determinant in powers of λ, it is evident that we have

$$\Delta = 1-\lambda N\sum_s\sum_r R_{sr}+\ldots .$$

The numerator takes the form

$$\sum_s -\lambda A_s \dot{N}\Delta_{ms}/\dot{N}_s,$$

where Δ_{ms} is the co-factor of the term in the mth column and sth row of Δ. For $m\neq s$ it will be seen that

$$\Delta_{ms} = -\lambda R_{sm}\frac{N\dot{N}_s}{\dot{N}_m}.$$

Except for the absence of the mth column and mth row, Δ_{mm} is of the same type as Δ; hence

$$\Delta_{mn} = 1-\lambda N\sum_s\sum_r(R_{sr}-R_{mr})+\ldots .$$

Accordingly

$$\omega_m = \frac{\lambda^2 N\sum\limits_s{}^{*}\dfrac{A_s N}{\dot{N}_s}\left(\dfrac{R_{sm}\dot{N}_s}{\dot{N}_m}\right)-\lambda\dfrac{A_m N}{\dot{N}_m}[1-\lambda N\sum\limits_s\sum\limits_r(R_{sr}-R_{mr})}{1-N\lambda\sum\limits_s\sum\limits_r R_{sr}},$$

where Σ^* indicates that the term $s=m$ is omitted. It is, however, clear that since $R_{mm}=0$, we may replace Σ^* by the general summation symbol over all s.

On writing

$$\frac{1}{1-N\lambda\sum\limits_s\sum\limits_r R_{sr}} = 1+N\lambda\sum_s\sum_r R_{sr}+\lambda^2,$$

we obtain, after evident reductions, equation (11).

A check on the accuracy of equation (11) is afforded if it be assumed that $\frac{A_s}{\dot{N}_s}$ is independent of s. It is clear that we should find

$$\omega = -\lambda \frac{A_m N}{\dot{N}_m} - \lambda^2 \frac{A_s N}{\dot{N}_s} \sum_s \frac{A_{sm} \dot{N}_s}{\dot{N}_m} A_{ms}$$

or

$$-\lambda \frac{A_m N}{\dot{N}_m} + \lambda^2 \left(\frac{A_m N}{\dot{N}_m} \right)^2$$

in agreement with equation (22).

XCVIII. *The Absorption of High-Frequency Radiation.* By EDMUND C. STONER, *Ph.D.* (*Cambridge*), *Reader in Physics, University of Leeds* *.

Introduction.

A NUMBER of formulæ have been put forward for the variation with wave-length of the absorption coefficient of high-frequency radiation. Before any of these formulæ can be applied with confidence, it is necessary to consider how far they are in agreement with experimental results on absorption. A simple direct comparison of theory and experiment is not at present possible, for the γ radiation, which is amenable to accurate experimental investigation, is heterogeneous. It is only for the γ-rays of RaB and C that data which are at all satisfactory are available for the intensity distribution, as well as for the wave-lengths; with these data, together with those on the mean absorption coefficient, it is possible to make a decision as to which of the absorption formulæ is in best agreement with experiment. It is perhaps premature to make this comparison, owing to the lack of finality in connexion with the intensity distribution; but it seems desirable to make a preliminary investigation, particularly in view of the fact that various formulæ have been used in deducing the wave-lengths of cosmic rays without any adequate ground for the view that they hold good even for the longer γ-rays. In this paper the intensity distribution given by Ellis will be modified in the light of his later work. Using different absorption formulæ, a calculation will then be made as to the mean absorption coefficient which would be deduced from experiments such as those of Ahmad, and the results compared with those he obtained. It will be seen that the experimental results are consistent with the Klein-Nishina relativistic formula, but not with the unmodified Dirac formula. This has an important bearing on the interpretation of the cosmic ray absorption results.

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* Communicated by Prof. R. Whiddington, F.R.S.

The Intensity Distribution of γ*-rays of* RaB *and* RaC.

An estimate of the intensities of the γ-rays from RaB and C has been made by Ellis and Wooster [*]. The method followed will be briefly indicated.

Let $V_1, V_2, V_3 \ldots V_n$ be the energies (proportional to the frequencies) expressed in volts of the γ-rays emitted; and let $p_1, p_2, p_3 \ldots p_n$ be the probabilities of emission, so that in N disintegrations there are emitted $Np_1, Np_2 \ldots Np_n$ γ-rays of energies $V_1, V_2 \ldots V_n$. For a γ-ray V_r, let ${}_K\alpha_r$ be the probability of internal conversion in the K level. Let $p_r\,{}_K\alpha_r = \theta_r$. Then, in N disintegrations, the number of electrons ejected from the K level by internal conversion of the γ-ray V_r is equal to $N\theta_r$. Now ${}_K\alpha_r$ will vary with the frequency of the γ-ray. Let g be the value for a standard γ-ray ($V = 3{\cdot}54 \times 10^5$ volts is taken), and for any γ-ray write

$${}_K\alpha_r = gf(V_r),$$

where

$$f(V_r) = 1 \quad \text{for} \quad V = 3{\cdot}54 \times 10^5 \text{ volts}.$$

The probability of absorption in the L, M ... levels, taken together, is approximately ·22 of that of absorption in the K level. Thus the total energy emitted from the atom, per disintegration, in the form of γ-rays (which have not been internally converted) is given by

$$E = \sum_1^n p_r V_r (1 - 1{\cdot}22\,{}_K\alpha_r)$$

$$= \sum_1^n \left[\frac{\theta_r V_r}{gf(V_r)} - 1{\cdot}22\,\theta_r V_r \right]$$

Ellis and Wooster consider 7 γ-rays from RaB ($V_1, V_2 \ldots V_7$) and 7 from RaC ($V_8, V_9 \ldots V_{14}$). In analogy with the external absorption coefficient, the internal absorption coefficient was taken to be slightly greater for RaC than RaB.

$$g_{\mathrm{RaC}} = 1{\cdot}03\, g_{\mathrm{RaB}}.$$

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[*] C. D. Ellis and W. A. Wooster, Proc. Camb. Phil. Soc. xxiii. p. 717 (1927).

It was also assumed that the internal absorption coefficient varied continuously as some power of the wave-length (or as some inverse power of V). Using the values of θ_r which may be deduced from the measurements on the β-ray group intensities, various powers of V are tried to see which gives results in closest agreement with the observed heating effect of the γ-rays (Ellis and Wooster [*]) and the observed number of γ-ray impulses (Kovarik [†]).

Let E be the γ-ray energy in the disintegration of 1 atom of RaB and 1 atom of RaC, and N the total number of impulses. The experimental data [‡] are as follows:—

$$E = 18{\cdot}4 \times 10^5 \text{ volts}, \quad E_{\text{RaB}} = 1{\cdot}44 \times 10^5, \quad E_{\text{RaC}} = 16{\cdot}96 \times 10^5,$$

$$N = 2{\cdot}14, \quad N_{\text{RaB}} = {\cdot}51, \quad N_{\text{RaC}} = 1{\cdot}63.$$

For the total number of impulses

$$N = \sum_1^7 \frac{\theta_r}{gf(V_r)} + \frac{1}{1{\cdot}03}\sum_8^{14} \frac{\theta_r}{gf(V_r)} - 1{\cdot}22\,\Sigma\theta_r\,;$$

while for the total energy

$$E = \sum_1^7 \frac{\theta_r V_r}{gf(V_r)} + \frac{1}{1{\cdot}03}\sum_8^{14} \frac{\theta_r V_r}{gf(V_r)} - 1{\cdot}22\,\Sigma\theta_r V_r.$$

It is convenient to consider the values for RaB and RaC separately, as this gives a more definite criterion in subsequent tests of the absorption formulæ tried; for the whole process essentially reduces to an estimation of the relative intensities of the high and low frequency components of the radiation. Inserting the numerical values given, the following four equations are then obtained:—

$$\text{Energy} \ldots\ldots \begin{cases} \displaystyle\sum_1^7 \frac{\theta_r V_r}{f(V_r)} = 2{\cdot}05\,g, & \quad (1) \\ \displaystyle\sum_8^{14} \frac{\theta_r V_r}{f(V_r)} = 17{\cdot}51\,g\,; & \quad (2) \end{cases}$$

$$\text{Impulses} \ldots\ldots \begin{cases} \displaystyle\sum_1^7 \frac{\theta_r}{f(V_r)} = {\cdot}68\,g, & \quad (3) \\ \displaystyle\sum_8^{14} \frac{\theta_r}{f(V_r)} = 1{\cdot}69\,g. & \quad (4) \end{cases}$$

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[*] C. D. Ellis and W. A. Wooster, Phil. Mag. l. p. 521 (1925).

[†] A. F. Kovarik, Phys. Rev. xxiii. p. 559 (1924).

[‡] The number of atoms disintegrating per second from 1 mg. is taken as $3{\cdot}4 \times 10^7$. The later result—$3{\cdot}68 \times 10^7$ (H. J. J. Braddick and H. M. Cave, P. R. S. cxxi. p. 367 (1928))—would reduce the value of g and the absolute intensities (Table III.) by a factor $3{\cdot}4/3{\cdot}68 = {\cdot}92$, but would not affect the relative intensities calculated.

In Table I. are given the values of λ, V, and θ for the 14 γ-rays considered. The values of θ (the intensities of the β-ray group due to K conversion of the γ-ray) for the RaC rays differ from those given by Ellis*, having been corrected in the light of later work by him and Aston† on the photographic action of β-rays.

TABLE I.

γ-ray Energies and β-ray Intensities.

	Number of γ-ray.	λ, 10^{-11} cm.	Energy, 10^6 volts.	θ.
RaB.	1	50·5	2·43	·0314
	2	47·3	2·60	·0038
	3	44·5	2·76	·0019
	4	41·6	2·97	·0435
	5	34·7	3·54	·0550
	6	26·2	4·71	·0008
	7	25·5	4·82	·0008
RaC.	8	20·1	6·12	·00380
	9	13·3	9·41	·00052
	10	10·9	11·30	·00132
	11	9·87	12·48	·00058
	12	8·62	14·26	·00318
	13	6·92	17·78	·00073
	14	5·55	22·19	·00018

For various assumed rates of variation of the absorption coefficient with the wave-length, values of g can be calculated from equations (1)–(4). The correct formula for $f(\mathrm{V})$ should give the same value of g in all four cases, provided the experimental results are correct. Dr. Ellis has kindly informed me that his later experimental results show that the variation with wave-length, as tested by a comparison of the internal with the external absorption, shows marked divergencies from continuity for the γ-rays 6·12 and $14{\cdot}26 \times 10^6$ volts. Although, in general, the internal absorption may be approximately represented by the formula $f(\mathrm{V}) = \mathrm{V}^{-x}$, for the 6·12 ray the absorption is about three times as small as this, and for the 14·26 about three times as great. Calculations of the value of g have been made, therefore, using the formulæ

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* C. D. Ellis and W. A. Wooster, Proc. Camb. Phil. Soc. xxiii. p. 717 (table i. p. 723) (1928).

† C. D. Ellis and G. H. Aston, Proc. Roy. Soc. cxix. p. 645 (1928).

$$f(\mathrm{V}) = \left(\frac{\mathrm{V}}{3{\cdot}54}\right)^{-x} \quad \text{for all } \gamma\text{-rays except 8 and 12,}$$

$$f(\mathrm{V}_8) = \frac{1}{3}\left(\frac{\mathrm{V}}{3{\cdot}54}\right)^{-x},$$

$$f(\mathrm{V}_{12}) = 3\left(\frac{\mathrm{V}}{3{\cdot}54}\right)^{-x}.$$

The values of x tried were 2·5, 2·6, and 2·7.
The results are shown in Table II.

Table II.

Calculated Values of g.

		$\mathrm{V}^{-2\cdot5}$.	$\mathrm{V}^{-2\cdot6}$.	$\mathrm{V}^{-2\cdot7}$.
Energy	RaB (1)	·160	·159	·158
	RaC (2)	·138	·159	·180
Impulses	RaB (3)	·148	·147	·146
	RaC (4)	·111	·123	·136

If the estimate of the division of energy between the γ-rays of RaB and RaC is approximately correct (Ellis and Wooster consider it is probably correct to 10 per cent.), the above figures indicate fairly definitely a rate of variation of absorption varying as $\mathrm{V}^{-2\cdot6}$. The results of the heating experiments, however, are not consistent with those of the counting experiments. The counting experiments, taken alone, would indicate a power considerably greater than 2·7; while if the results from the total number of impulses (RaB and C) are compared with the total heating effect, a power considerably less than 2·5 would be indicated—a result at variance with the ratio of the effects of RaB to RaC either in the counting or heating experiments.

On the whole, it seems that the heating experiments are less liable to give spurious results than the counting. If it is assumed that the internal absorption coefficient is equal to $\cdot159\left(\frac{\mathrm{V}}{3{\cdot}54}\right)^{-2\cdot6}$ in accordance with the heating results, the lower value of g for that power of V deduced from the number of impulses, indicates that the number of impulses counted is larger than the number of γ-ray quanta emitted from the atom; moreover, that the excess is greater in the case of the hard γ-rays from RaC than the softer rays from RaB. This is precisely what might be expected, if, as has been suggested, a high-speed photoelectron may give rise, by collision, to another fast electron. If the value ·159 for g is correct, the number of primary impulses (which actually escape from the atom) per disintegrating atom would be given by

$$N_{\text{RaB}} = \frac{\cdot 147}{\cdot 159} \times \cdot 51 = \cdot 47 \quad \text{(Observed } \cdot 51\text{)},$$

$$N_{\text{RaC}} = \frac{\cdot 123}{\cdot 159} \times 1{\cdot}63 = 1{\cdot}26 \quad \text{(Observed } 1{\cdot}63\text{)}.$$

In view of the uncertainties in the counting experiments, the general run of the internal absorption coefficient will be taken to be given approximately by the formula

$$\cdot 159\left(\frac{V}{3{\cdot}54}\right)^{-2{\cdot}6}$$

with the exceptions above mentioned for the lines $V = 6{\cdot}12$ and $V = 14{\cdot}26 \times 10^5$ volts. The values of p_r, the number of γ-rays per disintegration, and of $p_r V_r$, which is proportional to the intensity of the γ-rays, can then be calculated. These values, which are required for the calculation of the mean absorption coefficients, are given in Table III.

The Absorption of γ-Rays.

The absorption of the γ-rays from RaB and C has been comprehensively and carefully investigated by Ahmad *, whose results will here be considered. He found that the absorption per atom of the heterogeneous rays could be expressed by the formula

$$\mu_A = aZ + bZ^4,$$

where Z is the atomic number.

The first term was taken to be associated with scattering absorption, the second with photoelectric absorption. By assuming that b has the value that holds approximately in the X-ray region ($2{\cdot}29 \times 10^{-2}\lambda^2$) and that a was given by the Compton formula, the two values deduced for the "mean effective wave-length" were found to be in rough agreement. But it was pointed out that this was partly fortuitous, and it was concluded "that the wave-length as estimated from the scattering absorption by the Compton formula is too great." The essential value of Ahmad's work, however, was not due to its leading to a rough estimate of a mean wave-length, but to its showing that the absorption of γ-rays could be attributed to two distinct processes (as in the case of X-rays) and to its providing accurate data for the absorption coefficients under well-defined conditions.

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* N. Ahmad, P. R. S. cv. p. 507 (1924); cix. p. 206 (1925); (and E. C. Stoner) cvi. p. 8 (1924).

TABLE III.

Calculated Intensities of γ-Rays from RaB and RaC.

Number of γ-ray.	λ 10^{-1} cm.	p_r, No. of quanta per disintegration.	p_rV_r, 10^5 volts.
RaB. 1	50·5	·073	·178
2	47·3	·011	·028
3	44·5	·006	·017
4	41·6	·173	·510
5	34·7	·346	1·213
6	26·2	·011	·052
7	25·5	·012	·058
		$\sum_{1}^{7} p_r$ ·632	$\sum_{1}^{7} p_rV_r$ 2·056
RaC. 8	20·2	·295	1·81
9	13·3	·044	·41
10	10·9	·173	1·85
11	9·87	·036	1·20
12	8·62	·247	3·52
13	6·92	·305	5·42
14	5·55	·142	3·15
		$\sum_{8}^{14} p_r$ 1·302	$\sum_{8}^{14} p_rV_r$ 17·46

It will be most convenient for the present purpose to consider Ahmad's values for the scattering absorption per electron, σ. The final results for σ/σ_0 ($\sigma_0=6{\cdot}64\times10^{-25}$, the classical value) after filtering the rays, are shown in Table IV.

The above values include a correction of about 10 per cent. for the rays scattered forward into the ionization chamber. This correction is calculated from the estimated mean wave-length; but this means, effectively, that it is calculated so as to be consistent with the directly observed absorption, and it will not be greatly in error even if an incorrect scattering formula is used; so that the error introduced into the final value for the scattering will be very small.

TABLE IV.

Scattering per Electron for γ-Rays from RaB and C.

Filter.	σ/σ_0.
·5 cm. Fe	·327
2·5 cm. Fe	·315
6·5 cm. Fe	·312
1·0 cm. Pb	·298
3·4 cm. Hg	·297

The values obtained depend, of course, on the experimental arrangements—in particular, on the form of the ionization chamber used. This has long been recognized, but the problem, if attacked directly, becomes very complicated. A simple method will be given later by which a general idea may be obtained as to how far the deduced absorption coefficients are influenced by the ionization chamber factor.

Absorption Formulæ.

The scattering absorption formula made use of by Ahmad was that of Compton *.

$$\frac{\sigma}{\sigma_0}=\frac{1}{1+2\alpha},$$

$$\sigma_0=6\cdot 64\times 10^{-25},$$

$$\sigma=\frac{h\nu}{mc^2}=\frac{\cdot 0242}{\lambda}.$$

For this formula there was little theoretical justification, but it was useful as an empirical expression of the general nature of the variation of the scattering with wave-length.

On the basis of the quantum mechanics, Dirac † has given the formula:

$$\frac{\sigma}{\sigma_0}=\frac{3}{4}\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1+2\alpha}-\frac{1}{\alpha}\log(1+2\alpha)\right\}. \quad . \quad (5)$$

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* A. H. Compton, Phys. Rev. xxi. p. 483 (1923).

† P. A. M. Dirac, Proc. Roy. Soc. A, cxi. p. 423 (1926).

Klein and Nishina[*] have pointed out that Dirac's relativistic theory of the electron necessitates a modification of this formula (owing to the introduction of terms with $\left(\frac{h\nu}{mc^2}\right)^2$ in the formula connecting scattering with angle), and they give for the total scattering absorption:

$$\frac{\sigma}{\sigma_0}=\frac{3}{4}\left[\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1+2\alpha}-\frac{1}{\alpha}\log(1+2\alpha)\right\}\right.$$
$$\left.+\frac{1}{2\alpha}\log(1+2\alpha)-\frac{1+3\alpha}{(1+2\alpha)^2}\right]. \quad (6)$$

The difference in the numerical values given by these formulæ is illustrated by the figures in Table V. for wave-lengths in the range being considered.

TABLE V.

Scattering Absorption per Electron, σ/σ_0.

C, Compton; D, Dirac; K-N, Klein and Nishina.

λ, 10^{-11} cm.	α.	C.	D.	K-N.
48·4	·5	·50	·51	·56
24·2	1	·33	·35	·43
12·1	2	·20	·22	·34
6·0	4	·11	·13	·23

For homogeneous rays with the coefficient ·327 found by Ahmad, the three formulæ would give wave-lengths of about 23·6, 21·5, and $11·0\times10^{-11}$ cm. Calculation of the "mean wave-length" from Table V. $(\bar{\lambda}=\Sigma p_rV_r\lambda_r/\Sigma p_rV_r)$ gives a value of about 12×10^{-11} cm., which suggests that the Klein-Nishina formula is in closest agreement with the experimental results. But it is not legitimate to base any conclusions on this rough indication. The test of the Dirac and Klein-Nishina formulæ will now be considered in greater detail.

Test of Absorption Formulæ.

The question to be considered is the relation between the mean absorption coefficient for a heterogeneous beam found experimentally, and the absorption coefficients of the homogeneous constituents.

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[*] O. Klein and Y. Nishina, 'Nature,' cxxii. p. 398 (1928).

Let I_0 be the initial intensity of the beam.

$$I_0 = I_1 + I_2 \ldots + I_r + \ldots = \Sigma I_r.$$

If the absorber is not too thick—in Ahmad's experiments the thickness was chosen so that about 20 per cent. of the radiation was absorbed—the decrease in intensity in passing through a thickness δx is given by

$$\delta I_0 = \bar{\mu} I_0 \, \delta x = (\Sigma \mu_r I_r) \, \delta x.$$

If the ionization chamber absorbs all the radiation completely in such a way that the ionization current is directly proportional to the intensity of the radiation, the ordinary mean absorption coefficient will be deduced from the experiments.

$$\mu = \frac{\Sigma \mu_r I_r}{\Sigma I_r} = \frac{\Sigma \mu_r I_r}{I_0}.$$

Ahmad's experiments enabled the scattering absorption coefficient to be separated from the photoelectric absorption coefficient. The value of the scattering coefficient per electron $(\bar{\sigma})_1$, which would be deduced if the above conditions held, is given by

$$(\bar{\sigma})_1 = \frac{\Sigma I_r \sigma_r}{I_0}.$$

Since I_r is proportional to $p_r V_r$ (see Table V.), this may be written:

$$\overline{\left(\frac{\sigma}{\sigma_0}\right)_1} = \Sigma p_r V_r \left(\frac{\sigma}{\sigma_0}\right)_r \Big/ \Sigma p_r V_r. \quad . \quad . \quad . \quad . \quad (7)$$

This expression gives a limiting value which would be deduced if the ideal conditions could be realized.

Now, suppose that the ionization chamber absorbs only a fraction of the incident radiation, and, as before, that the ionization current is proportional to the amount absorbed. Let l be the length of the chamber, μ_r' the absorption coefficient for the rth constituent of the radiation. The initial intensity, I_0', then measured would be

$$I_0' = \Sigma I_r (1 - e^{-\mu_r' l}).$$

The measured absorption coefficient (of the absorber) would be given by

$$\begin{aligned} \bar{\mu} &= \frac{1}{I_0'} \frac{\delta I_0'}{\delta x} \\ &= \Sigma \mu_r I_r (1 - e^{-\mu_r' l}) / \Sigma I_r (1 - e^{-\mu_r' l}). \end{aligned}$$

In the limiting case, when $\mu' l$ is small, this gives

$$\bar{\mu} = \Sigma\mu_r\mu_r' \mathrm{I}_r / \Sigma\mu_r' \mathrm{I}_r.$$

For the scattering absorption per electron,

$$\overline{\left(\frac{\sigma}{\sigma_0}\right)}_2 = \Sigma p_r \mathrm{V}_r \left(\frac{\sigma}{\sigma_0}\right)_r \mu_r' / \Sigma p_r \mathrm{V}_r \mu_r'. \quad . \quad . \quad . \quad (8)$$

This gives a second limiting case.

The conditions necessary for the application of either of these equations are not satisfied, but are intermediate.

In Ahmad's later experiments the ionization chamber was about 15 cm. long, and contained lead plates of aggregate thickness 1·05 cm. His experiments show that there is about 54 per cent. absorption of the radiation in passing through 1 cm. of lead. While the longer wave-length radiation is almost completely absorbed, probably only about 20 per cent. of the shortest wave-length radiation will be. As far as the absorption in the ionization chamber is concerned, therefore, the conditions are intermediate between those required for equations (7) and (8).

A difficulty arises in that whereas the ionization current in a gas (due almost entirely to the recoil electrons produced in the Compton scattering process) may be taken as proportional to the absorption, much of the absorption in the lead plates gives rise to no ionization current, but simply results in heating. The question is of importance in the choice of the best value of μ' in equation (8). The values of μ' are proportional to the absorptions per electron, and if these were the same for air and lead, the question of choice would not arise. But for lead an appreciable part of the absorption for the long wave-lengths is due to photoelectric absorption; only a fraction of this, however, will add to the ionization current; so that the calculations will be made using (*a*) μ_e for air, (*b*) μ_e for lead.

The value of μ_e is given by

$$\mu_e = \sigma + \tau.$$

σ may be calculated for different wave-lengths, using the Dirac, or Klein-Nishina, formula. τ will be taken as

$$\tau = 2{\cdot}29 \times 10^{-2} \lambda^3 \mathrm{Z}^3.$$

This is, of course, an extrapolation from the X-ray results, and is probably sufficiently correct for the present purpose.

In Table VI. are given the values which would be deduced for the mean (σ/σ_0) for a heterogeneous beam with the intensity distribution of Table V., using the Dirac and Klein-Nishina formula. The values are calculated from the following formulæ :—

$$(\sigma/\sigma_0)_1 = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\Big/\Sigma I_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$(\sigma/\sigma_0)_{2a} = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\mu'_{ar}\Big/\Sigma I_r\mu'_{ar}, \quad \text{where } \mu'_a = \mu_{air},$$

$$= \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)^2\Big/\Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right), \quad . \quad . \quad . \quad . \quad . \quad (8\,a)$$

$$(\sigma/\sigma_0)_{2b} = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\mu'_{br}\Big/\Sigma I_r\mu'_{br}, \quad \text{where } \mu_b = \mu_{Pb},$$

$$= \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\left(\frac{\mu_e}{\sigma_0}\right)_{Pbr}\Big/\Sigma I_r\left(\frac{\mu_e}{\sigma_0}\right)_{Pbr} \quad . \quad . \quad . \quad (8\,b)$$

TABLE VI.

Calculated and Observed Mean Absorption Coefficients.

	Dirac (5).	Klein-Nishina (6).
$(\sigma/\sigma_0)_1$ from (7)	·203	·308
$(\sigma/\sigma_0)_{2a}$ from (8 *a*)	·253	·331
$(\sigma/\sigma_0)_{2b}$ from (8 *b*)	·325	·382
$(\sigma/\sigma_0)_2$ Mean	·289	·356
Mean $\frac{1}{2}(\sigma/\sigma_0)_1+\frac{1}{2}(\sigma/\sigma_0)_2$......	·246	·332
Observed	·327	

The observed value tabulated is that obtained after the rays had been filtered through ·5 cm. iron. Without filtering, rough extrapolation indicates that the observed value would be about 2 per cent. higher than this. The mean value calculated using the Klein-Nishina formula agrees remarkably well with that observed. The observed value is incompatible with the unmodified Dirac formula.

Effect of Filters.

As the absorption in the ionization chamber of the unfiltered rays is about 50 per cent., the method of calculating a mean value as above seems justifiable, but it would be expected that, as the rays are progressively hardened by filters, the observed absorption would tend towards the value calculated using (8) rather than (7). Some calculations were therefore made as to the mean absorption coefficients which would be deduced after the rays had been filtered through ·5, 1·5, and 6·5 cm. iron, 1 cm. lead, and 3·41 cm. mercury, as in Ahmad's experiments. The intensity of a ray after passing through a thickness x of a substance is given by

$$I_r = (I_r)_0 \, e^{-\mu x}.$$

Let μ_e be the absorption coefficient per electron.

$$\mu = \frac{N\rho}{A} Z \mu_e$$

where $Z =$ atomic number, $\rho =$ density,
$A =$ atomic weight, $N = 6{\cdot}06 \times 10^{23}$
$\mu_e = \sigma + \tau = \sigma + 2{\cdot}29 \times 10^{-2} \lambda^3 Z^3.$

The intensity of each of the rays was calculated using the Klein-Nishina formula for σ, and the mean values of the absorption coefficients after filtration estimated as before. The results are shown in Table VII.

As the beam is progressively filtered, owing to the variation in the absorption coefficient with wave-length, there will be an increase in homogeneity. and the beam will eventually be composed mainly of only the shortest wave-length radiations of those initially present (see Table V.). For the three shortest—$\lambda = 8{\cdot}62$, $6{\cdot}92$, $5{\cdot}55$—the values for (σ/σ_0) are ·286, ·250, and ·216 ; so the values calculated for the beam after filtration through 6·5 cm. iron and 3·41 cm. mercury (·269 and ·262) are of the order of magnitude to be expected. It would be expected, then, that as the filters

TABLE VII.

Calculated and Observed Values of $(\sigma/\sigma_0) \times 10^3$.

Filter.	—	0·5 cm. Fe.	2·5 cm. Fe.	6·5 cm. Fe.	1 cm. Pb.	3·41 cm. Hg.
$(\sigma/\sigma_0)_1$ from (7)	308	300	281	260	276	260
$(\sigma/\sigma_0)_{2a}$ from (8 *a*)	331	324	301	272	286	265
$(\sigma/\sigma_0)_{2b}$ from (8 *b*)	382	364	326	285	300	265
$(\sigma/\sigma_0)_2$ Mean	356	344	313	278	292	265
Mean $\frac{1}{2}(\sigma/\sigma_0)_1 + \frac{1}{2}(\sigma/\sigma_0)_2$ ...	332	322	297	269	284	262
Observed	(333)	327	315	312	298	207

increase in thickness, the measured value of (σ/σ_0) would tend to a limiting value, and that this would agree more closely with that calculated from equation (8), corresponding to partial absorption in the ionization chamber, than from equation (7), corresponding to complete absorption. This tendency to a limit is observed with iron, the value with 6·5 cm. (·312) being only slightly less than with 2·5 cm. (·315); and also when 3·41 cm. mercury is substituted for 1 cm. lead (·297 and ·298). But the numerical values observed with thick filters are much greater than those calculated. The calculated "hardening effect" of the lead filter is actually less than that of the thick iron filter, and that of the mercury only slightly greater; while the observed hardening of the lead and mercury, though less than that calculated, is much greater than that of iron.

No obvious explanation of these discrepancies suggests itself. If the absorption coefficient for the shorter wave-lengths was greater than that calculated from the Klein-Nishina formula, some of the discrepancies would be removed, but the difference in the observed effect of mercury and iron would still be unexplained. It may be that, owing to the scattered radiation being concentrated in a forward direction, a certain amount of scattered radiation accompanies the beam, so that its effective mean wave-length, and scattering coefficient, is greater than that calculated; and that then the photoelectric absorption in lead and mercury, owing to its more rapid variation with wave-length, accounts for the increased hardening effect of these elements. (The value of τ/σ for lead varies from about $\frac{1}{8}$ to $\frac{1}{70}$ as λ varies from 13·3 to 5·5). It does not, however, seem desirable to speculate too much until the intensity distribution of the γ-rays is known with greater certainty.

In Ahmad's experiments a strictly parallel beam was not used, and as it is a matter of some difficulty to correct for scattering, it seems not improbable that scattering effects may play a rôle in the manner suggested. In some experiments by Kohlrausch*, a parallel beam was used, and the results were analysed so that effectively the final values corresponded to rays filtered through 4 cm. lead. He found that the absorption coefficient of the rays after filtration through about 4 cm. lead tended to a limiting value—the values found being $\mu=\cdot126$ in Al, $\mu=\cdot533$ in Pb. These values correspond to values for (μ_e/σ_0) of ·241 and ·295 respectively. The value ·241, which may be taken as equal to (σ/σ_0), is in good agreement with the value for the hardest components given by the Klein-Nishina formula (·286, ·250, and ·216). There can thus be little doubt that the Klein-Nishina formula is experimentally justified in the range of wave-lengths considered, and that the anomalous results with filters are due to secondary effects.

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* K. W. F. Kohlrausch, *Phys. Zeits.* xxviii. p. 1 (1927).

Discussion.

The main conclusion to be drawn from this investigation is that if the variation of the electron scattering coefficient with wave-length is that given by the Klein-Nishina formula, the results of the experiments from which the intensity distribution is estimated are consistent with those of the absorption experiments. For the unfiltered rays of RaB and C, the absorption coefficient estimated using the unmodified Dirac formula is about 25 per cent. lower than that observed; using the Klein-Nishina formula, there is agreement to within 2 per cent. This result is obtained when what seems to be a reasonable estimate of the efficiency of the ionization chamber is made.

It has, of course, long been realized that the results of absorption measurements with heterogeneous short wave-length radiation depend considerably on the ionization chamber used. The calculations which have been made indicate, by the consideration of limiting cases, the range of indefiniteness. In absorption experiments of this kind, a careful study of the characteristics of the ionization chamber is necessary. If the intensity distribution is known it should be possible to make a precise test of any absorption formula by choosing the ionization chamber suitably. The usual practice has been to use an ionization chamber which absorbs the radiations almost completely. This would be an ideal arrangement if the ionization current were strictly proportional to the absorption. This, however, is generally not the case. It would seem, therefore, better to use an ionization chamber in which the ionization current is closely proportional to the absorption, say a gas-filled chamber. Significant results would then be obtained if the fractional absorption were small. Then, if I_r is the initial intensity of the rth radiation, μ_r and μ_r' the absorption coefficients of the absorber and of the substance in the ionization chamber, the mean measured absorption coefficient would be given by

$$\bar{\mu} = \Sigma I_r \mu_r \mu_r' / \Sigma I_r \mu_r'.$$

An obvious elaboration of this method would be to make measurements with two ionization chambers of different lengths. Corrections could then be made for the effects of the walls, which have recently been investigated, with electroscopes, by Chalmers *.

One of the most interesting applications of the absorption formulæ is to the determination of the wave-lengths of cosmic-rays. By analysing his depth-ionization curve, Millikan † finds that it can be accounted for by the presence of three approximately homogeneous groups of rays with absorption coefficients in water of ·35, ·08, and 0·4 metre^{-1}, corresponding to wave-lengths, with the Dirac formula, of about ·5, ·11, and $\cdot 06 \times 10^{-11}$ cm. The absorption per electron is related to the mass absorption by the formula

$$\sigma = \frac{\mu}{\rho} \times \frac{A}{NZ}$$

(μ is the absorption coefficient in cm.$^{-1}$, A and Z are the atomic or molecular weight and number, $N = 6{\cdot}06 \times 10^{-23}$).

For water ($\rho = 1$, $A = 18$, $Z = 10$) in which the photoelectric absorption is negligible, this gives

$$(\sigma/\sigma_0) = \frac{1}{\sigma_0} \frac{18}{10N} \mu = 4{\cdot}48\, \mu.$$

The calculated wave-lengths, using the two formulæ, are given in the following table :—

Calculated Wave-lengths of Cosmic Rays.

μ_{H_2O}. Metre^{-1}.	$\frac{\sigma}{\sigma_0}$.	$\lambda \times 10^{11}$ cm.	
		Dirac.	Klein-Nishina.
·35	·0156	·535	·161
·08	·00358	·117	·029
·04	·00179	·059	·013

These values may be compared with those corresponding to the upbuilding of atoms from protons and electrons, as suggested by Millikan, and the "annihilation" wave-length, corresponding to the conversion of the intrinsic energy of a proton into radiational energy.

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* J. A. Chalmers, Phil. Mag. vi. p. 745 (1928).

† R. A. Millikan and G. Cameron, Phys. Rev. xxxi. p. 163 (1928); xxxi. p. 921 (1928); xxxii. p. 533 (1928).

Calculated Wave-lengths for Different Processes

		$\lambda \times 10^{11}$ cm.
Upbuilding	He	·46
	N	·133
	O	·107
	Si	·057
Annihilation		·013

Using the Dirac formula, the smaller absorption coefficients do correspond to the upbuilding of nitrogen or oxygen (or both) and of silicon, but the agreement in the case of helium can hardly be regarded as satisfactory. There are strong reasons, which have been considered elsewhere *, for regarding Millikan's explanation of the origin of cosmic rays as highly improbable. Now that the Klein-Nishina formula has been shown to be consistent with the γ-ray results, while the Dirac formula is unsatisfactory, there is definite justification for using the modified formula for the cosmic rays. The revised wave-lengths could, of course, still be accounted for by the upbuilding of some atoms, but these would no longer be the most abundant ones; and the fact that the atoms required were abundant was considered to be a strong point in favour of the upbuilding explanation.

The absorption coefficient ·04 metre^{-1} does now correspond to the annihilation wave-length. Moreover, the scattered radiation is concentrated in a forward direction, and, as has been shown by Millikan, the mean wave-length is approximately twice that of the incident radiation. Thus the absorption coefficient ·08 ($\lambda = \cdot 029$) may well be accounted for by the secondaries due to the annihilation wave-length radiation. The origin of the most strongly absorbed radiation, however, still remains obscure. Its relatively great intensity would appear to indicate that it is not to be explained by some secondary effect of the more penetrating radiation in any of the ways which have been considered.

There is very strong astronomical evidence for the view that mutual annihilation of electrons and protons must in some way occur. The objection that there is no indication of the corresponding radiation in the cosmic ray depth ionization curves now seems to be removed.

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* E. C. Stoner, Proc. Leeds Phil. Soc. i. p. 349 (1929).

Summary.

A revised estimate of the intensities of the γ-rays of RaB and C has been made using the results of Ellis on the β-rays and on the γ-ray heating effect. If these results are correct, it is shown that the number of impulses counted by Kovarik is greater than the number of γ-ray quanta emerging from the disintegrating atoms.

The absorption coefficient which would be deduced with an experimental arrangement such as that of Ahmad is then calculated, using the Dirac and Klein-Nishina formulæ. The values obtained are in close agreement with the Klein-Nishina formula. The unmodified Dirac formula gives values about 25 per cent. too low.

The effect of filters is considered. Some of Ahmad's results appear anomalous, probably on account of secondary scattering effects. Kohlrausch's results with thick filters are consistent with the modified formula.

Suitable experimental arrangements for more precise tests of the formulæ are briefly discussed.

With the Klein-Nishina formula the most penetrating cosmic radiation observed by Millikan corresponds to the electron-proton annihilation wave-length.

Physics Department,
The University, Leeds.
January 1929.

XCIX. *The Raman Effect by Helium Excitation.*

By R. W. Wood *.

[Plate XXI.]

THE improved method of irradiating fluids by the light of the mercury arc, for the excitation of the Raman lines of modified wave-length, which I described in this Journal for Oct. 1928, has been still further improved, and though I have now abandoned the mercury arc for the helium lamp, which yields spectra excited by a pure monochromatic radiation, I think that a brief description of the new modification may prove helpful to workers in the field who lack facilities for the excitation by helium.

The disadvantage of the water-cooled tube which I described in the earlier paper was the necessity of using a large volume of an absorbing medium in a pail for supplying the cooling system in cases in which it was desired to suppress one or the other of the mercury lines. This was especially troublesome in the case of a solution of cobalt sulphocyanate, which I found much more effective in suppressing the 4358 group than a solution of fluorescein. The solution has to be very concentrated, however, and

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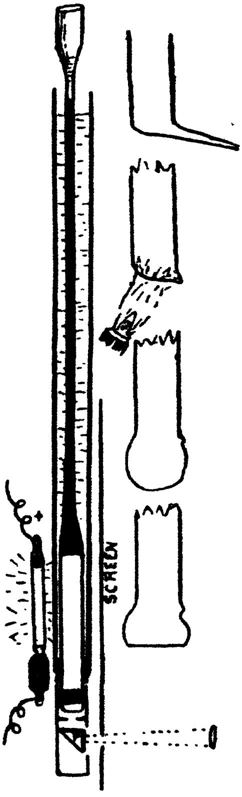
* Communicated by the Author.

Fig. 1.



I accordingly designed the cooling system shown in fig. 1, which accomplishes the desired result with a few hundred centimetres of fluid. The outer tube, preferably of thin pyrex glass, is 50 cm. long and has a diameter of 5 cm. The inner tube, with a diameter of 3·5 cm., is drawn down as shown in the figure, the portion indicated being painted with black "Duco" auto-enamel (a celluloid paint). The bottom of the tube is flattened, avoiding a lenticular button in the centre, and the outer surface ground flat and polished. A flattened bulb, if properly made, acts quite as well, but is easily broken. The bulb should be blown in the stages shown in fig. 1, to secure an optically flat bottom. It should be very thin, and in flattening the bottom a vertical flame must be used, such as a Bunsen flame turned down very low, the tube being held in the vertical position. A round bulb cannot be used, as it acts as a short-focus lens when the tube is filled with liquid. The inner tube passes through a rubber gasket made from a stopper by cutting the ring out with a penknife while the stopper is spun with a lathe (see Phil. Mag. for Oct.). It is filled with the fluid to be observed to the upper end of the narrow portion, the widened top taking care of expansion. A cylinder of thin polished sheet aluminium is slipped around the lower part of the tube, embracing about two-thirds of its circumference, to serve as a reflector, and the outer tube then put in position, pressing the rubber gasket well into place, and securing it with thin copper wire. The space between the tubes is then filled with water or an absorbing solution, and the vertical quartz mercury arc mounted close to the wall, opposite the window in the aluminium reflector.

The cooling is effected by convection and radiation. With an apparatus of the dimensions given the temperature will come to rest at about 70° if the lamp is placed very close to the outer wall. In the case of liquids with boiling-points below 80° the lamp can be moved away a centimetre or two. Great care must be used with liquids having very low boiling-points, such as ether. It is well to keep a thermometer in the water, and move the lamp off as may be necessary. It is very important to screen the spectroscope from all rays except those issuing from the bottom of the tube, as by the method shown in fig. 1, in which the reflecting prism is contained in a black tube with suitable apertures and diaphragms. With an apparatus of this description one can photograph the stronger Raman lines with a small constant deviation spectroscope in two or three minutes. It can be operated without attention for hours or even over night, when using high dispersion. But at best the mercury arc is a very unsatisfactory source, owing to the impossibility of isolating a strictly monochromatic radiation from it.

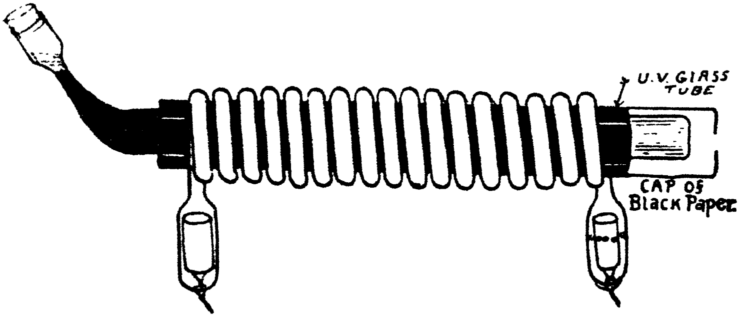
The close group of three lines at 4340–4358 yields a complicated spectrum, and the lines excited by 4046–4077 cannot be separated until all wave-lengths are measured, converted into frequencies, and the frequency differences compared.

It occurred to me that if a pure monochromatic excitation could be devised one might avoid all wave-length measurements and computations, for it would be necessary only to prepare a scale properly graduated to represent the infra-red wave-lengths associated with the Raman lines, and then enlarge the spectrogram to a suitable degree to fit the scale, and place the two in register. The infra-red wave-lengths could then at once be read off from the scale at each Raman line.

This cannot be done with the spectra made with the mercury arc for the reasons just given.

After considering all possible sources, I finally chose the helium vacuum tube as the most suitable, for the 3888·6 line is about 80 times as intense as any line in its immediate vicinity when filtered by nickel oxide glass and all visible radiations are cut off. In preparing large blown cylinders of this glass during the war, for making ultra-violet "running lights" for ships in convoy, I had a few of them drawn out into long tubes, thinking that possibly Cooper-Hewitt lamps could be made of them. The tubes have been lying about my laboratory ever since, waiting for possible service. They proved to be exactly what I wanted. The tube containing the fluid under examination is slipped into the tube of nickel oxide glass and surrounded by a spiral tube provided with electrode bulbs and filled with helium at 8 mm., and excited by a 20,000-volt transformer.

Fig. 2.



The spiral discharge tube is cooled by an electric fan placed close to it, and I have had no difficulty in working with fluids boiling at 40°, the tube running over night without attention.

The ultra-violet glass transmits the light of the 3888 line at almost its full intensity, and to a much less degree the lines 3965 and 4025, but these are so feeble that I have never found a Raman line that could be attributed to them. The only disadvantage of their presence is that they may occasionally mask a Raman line that happens to coincide with them. Another advantage is that the entire Raman spectrum falls in a spectrum range over which the photographic plate shows nearly uniform sensitivity. With mercury 4358 excitation the lines corresponding to 3 μ absorption fall at about wave-length 5000, the region of minimum sensibility. In the case of the benzene, toluene, xylene, and similar compounds these lines are by far the strongest lines of the whole spectrum, while Raman listed the intensity as 1 on a scale of 10 for excitation by Hg 4358, which is precisely what one gets, even with a so-called orthochromatic plate. The presence of the other two helium lines on the plate is an advantage in one way, in that it aids one in fitting the photograph to the scale.

The 3888 line is so broadened by over-exposure that the setting must be done for this line by the edge of the spectrum corresponding to the end of the slit, where the broadened line comes to a blunt point.

The helium tube (of 10 mm. diameter) has a total length of 3 metres, but is wound into a spiral 6·5 cm. in diameter and 25 cm. in length. It was constructed by the Claude Neon Light Co. of Baltimore, and has cylindrical copper electrodes, which were very thoroughly outgassed before filling. After some two hundred hours of operation the tube has "gone-hard," and refuses to conduct. I am not at all sure of what has become of the 8 mm. of helium which it contained. The commercial tubes apparently do not give this trouble, but they are made of a yellow glass which would be quite unsuitable for 3880 transmission.

Spectra obtained with this apparatus of the lower alcohols and a number of benzene substitution compounds, including the three isomers of xylene and methyl cyclo-hexane, are reproduced as negatives on Pl. XXI.

The μ-scale is at the top, the graduations of which run all the way down the sheet, so that the infra-red absorption line corresponding to any Raman line can be read off at once. A scale of wave-lengths is added at the bottom.

The μ-scale was prepared in the following way. A photograph of the iron and helium spectra superposed was made with the prism spectrograph used for making the Raman spectrograms (a small ancient model of Hilger's constant deviation fitted with a home-made plate-holder).

This was enlarged five-fold on a lantern-slide plate, which was in turn enlarged five-fold on a strip of bromide paper. The spectrum thus obtained from helium 3888 (the exciting-line used) to helium 4471 (the end of the Raman spectrum) measured 35 cm. in length, and the Raman spectra were enlarged to the same scale in the same way. Plate XXI. has been reduced about one-half from the original enlargements.

A scale of wave-lengths was prepared for the iron spectrum, and the wave-lengths were then calculated (from Kayser's table of frequencies), which corresponded to 3 μ, 3·1 μ, 3·2 μ, etc., up to 100 μ, by which we mean that the frequencies corresponding to these wave-lengths, when subtracted from the frequency of the helium 3888·6 line, give the frequencies corresponding to the divisions required for the μ-scale.

Tenths were calculated only up to 8 μ, and above this as shown by the scale on the plate.

The values thus obtained were carefully marked on the wave-length scale, these marks giving the graduations of the μ-scale.

Having once prepared our scale we can determine immediately the wave-lengths of the infra-red absorption bands corresponding to the Raman lines by simply fitting the enlarged photograph to the scale. The enlargements should all be made on the same type of paper, and dried in the same way to avoid unequal shrinkage.

The values read off on the plate show slight errors, as it is difficult to mount a number of dry prints and not have some small expansions and contractions. For quantitative work I should be disposed to make a more accurate one than the one reproduced, which was a first attempt, and made in a hurry.

The advantage of the new method of excitation, and this short cut to the μ-values, will be obvious to anyone who has spent a whole day or more in measuring up a single Raman spectrum, computing the wave-lengths, looking up the frequencies, making the subtractions, and then searching out the lines which have a common excitation.

An alternative method, which would give results of greater accuracy and involve not much more time, would be to prepare a scale on which readings of the comparator were plotted against the μ-values, the scales being in coincidence. One would then merely mount the spectrogram in the comparator (set to zero say), and bring the helium exciting line on the cross-hairs. As each Raman line comes on the cross-hair we take the reading and find the μ-value which corresponds to it on the double scale.

The original spectrograms from which Pl. XXI. was made were extremely sharp, but the total length of the spectrum was only 10 mm. I was unable to use my Bausch and Lomb spectrograph in the case of the helium excitation on account of the strong absorption of its prism for wave-lengths below 4050. The prism in the smaller Hilger instrument showed good transparency to below the exciting helium line.

I am having a new prism made for the B. and L. instrument, as a 25-fold enlargement puts too much of a strain on the enlarging apparatus for the finest detail. This was especially noticeable in the complicated groups of lines which correspond to the 3·4 μ region. These groups I enlarged over again, first with a low-power microscope and then with the enlarging camera. They have been pasted over the poorly-defined images on the plate in the case of the benzene and related compounds. If this plate is compared with the one illustrating my paper in the Oct. 1928 number of this Journal, the enormous advantage of the helium excitation is at once apparent. We see immediately that the strong triple line of ethyl alcohol was excited by Hg 4046, while the line to the right of it was excited by 4358 corresponding to the line at 6·8 μ by helium excitation. The line to the left of the triple line I have not yet reconciled with the helium photograph, for it does not appear in the methyl alcohol spectrogram. This matter will be further investigated.

The ease with which mistakes are made in the case of excitation by the mercury arc is illustrated by an example taken from Pringsheim's paper on the Raman effect (*Zeit. f. Physik*, l. p. 742).

In the first column of his table he gives the Raman line 4659 of benzene as excited by 4359, and also by 4078. In my earlier paper this line was referred to 4078 excitation, as it did not appear on plates made by mercury arc light from which the group 4046–4077 had been removed by a filter of potassium chromate. Pringsheim evidently assumed that it was excited also by 4358, as in this case it would be identified with the absorption band at 6·75 μ found by Coblentz, which is the heaviest absorption band of benzene. The helium excitation confirms my earlier assignment of the line, for there is not the slightest trace of a line at 6·75 μ, showing that the strongest absorption band of benzene is not represented at all in the Raman spectrum.

The spectrum of benzene was photographed with the B. and L. spectrograph, with a rather long exposure to ascertain the nature of the companion lines which border the 4407 line (3·3 μ). As I showed in a short note published in this Journal for Dec. 1928, this line is in reality double—a strong component about 1 Å.U. in width, bordered on the short wave-length side with a fainter broad companion. The photograph was made with a lens of 3-metre focus combined with a large plane grating of 6 in. diameter.

These companions were found to have the same structure as the very intense double line which they accompanied. A microphotometer curve was made for me on the Moll instrument at the Naval Research Laboratory, and is reproduced on Pl. XXI. I have put black dots under the companions. The faint line to the left is a very strong helium line, 4471, which probably reached the slit from the walls of the room. The dual nature of the main line was mostly obscured by over exposure, but it is very clear in the companions, which resemble two first- and one third-order "ghosts" of the main line (to use grating nomenclature). The photograph was made with a prism, however. It seems probable that these companions are related in some way to main lines. They appear unresolved on the benzene spectrum on the plate. To get them by combination we should have to have an absorption band at about 95 μ, and no Raman line appears at this point.

After working a month with helium excitation I should never think of returning again to the mercury arc. The question which the reader will ask is, of course, "How about getting tubes of nickel glass?" The only answer that I can give is that I am trying at the present time to induce some one or more of the glass manufacturing companies to prepare tubing of this glass.

The glass which I made during the war seems to be rather superior to that which is on the market in America, having a sharper cut-off. I am now setting up an apparatus in which the illumination is to be by one of the new hot-cathode helium lamps (operating on 220 volts) developed in the research laboratory of the General Electric Co., and I am under great obligation to Drs. Whitney and Dushman, who furnished me with one of these lamps. The time of exposure will probably be much less than that required with the helium spiral, with which I give from five to fifteen hours.

The object of the present paper is to acquaint those who are working on the Raman effect with the new technique which I have employed, as an enormous amount of time is lost in working with the mercury arc. A discussion of lines in their relation to chemical constitution will be deferred to a subsequent paper. A photograph such as the one reproduced will be a great help, as one can see at a glance the changes resulting from altering the structure of the molecule.

Prof. E. C. Kemble and Dr. E. L. Hill, of Harvard University, have worked out the quantum mechanical theory of the effect for HCl accounting for the sharpness of the single line, and the lines identified with alternate lines of the pure rotation band in the remote infra-red. Their paper will appear shortly in the Proc. Nat. Acad.

C. *The Effect of Ultra-Violet and X-Rays on the Steady Current Characteristics of Crystal Detectors. By* W. Jackson, *M.Sc., Lecturer in Electrical Engineering, Technical College, Bradford* [*].

Introduction.

MANY theories have been put forward to explain the action of the crystal detector, but as yet no one of them has been accepted as completely satisfactory. As was the earlier coherer, this extremely sensitive detector, before being thoroughly understood, has been largely superseded by more reliable and stable methods of rectification. The gradual accumulation of data will, no doubt, in time lead to a theory capable of embracing and explaining the many phenomena which have been observed and recorded in published work on crystal detectors.

Dr. Eccles [†] has put forward a theory based on thermoelectric action at the light contact of the detector. It is supposed that the passage of current across the high-resistance junction of the two dissimilar metals or metallic compounds causes heat to be produced, and the local heating leads to the generation of a thermoelectric E.M.F. These thermal actions are very noticeable in contacts made of the badly conducting natural oxides or sulphides used in crystal detectors. This thermoelectric E.M.F. occurs during both the positive and negative half-cycles of the applied alternating voltage producing the current, during one of which it assists and during the other opposes, giving the phenomenon of asymmetric conduction. Complete rectification can only

[*] Communicated by the Author.

[†] Proc. Physical Soc. xxii. pp. 360 & 477 (1910); xxv. part iv. p. 273 (1913).

result when, during one half-cycle, the applied and thermoelectric E.M.F.'s accurately balance.

A. C. James* has attempted to substantiate the early electrolytic theories of crystal rectification. He suggests that the passage of a direct current through galena (the crystal under his investigation), the negative contact being a metallic point, is accompanied by the electrolytic formation of metallic threads across the contact; while, when the point is positive, a high resistance film is formed. He explains the unidirectional conductivity and rectification from a consideration of the crystal structure, and by the fact that in solid electrolytes the current is carried entirely by one set of ions, the other forming a fixed framework. In rectification the metal ions are supposed to oscillate to and fro through fixed channels in the high-resistance film, giving metallic and non-metallic contact alternately during the two half-cycles of the applied E.M.F. The reason given for the variation of the rectifying properties at different points on the crystal surface is that the metal ions can move without collision in some planes of the crystal, but not in others.

A more recent theory put forward by W. Ogawa † states that the rectification is brought about by the difference of electron emissions from the two electrodes forming the contact, and that thermoelectric and electrolytic effects do not enter into the question. He shows that rectification is possible by two electrodes of different electron emissions separated *in vacuo* in the cold state, and that the direction of the rectified current is the same as that in a contact detector composed of the same electrode materials. In effect the crystal is a cold vacuum-tube operating as a detector by the differences in electronic emissions of its electrodes.

L. S. Palmer ‡ suggests that this analogy with the thermionic valve is supported by the observed phenomena that improved rectifying properties are obtained when the tendency for electronic emission is increased. Most crystals exhibit increased rectifying efficiency when a small steady potential is applied across the contact of such polarity as to produce a current in the same direction as the rectified current. A similar effect has been noticed when the crystal contact is heated.

The result of adding a small quantity of impurity is to improve the rectification, and suggests that the impurity increases the electronic emission from the crystal. That certain faces of the crystal appear to be better than others as regards rectification may be explained by this if the points of maximum rectification are found where thin layers of impurities, included in the crystal during the process of formation, exist. This seems likely since the purest crystals exhibiting normal crystalline form show no very sensitive spots, while those exhibiting variation in form from the normal usually have many [*]. These phenomena seem to indicate that the rectifying properties of a substance may be expected to be appreciable if the work necessary to remove an electron is small [†].

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* Phil. Mag. xlix. p. 681 (1925).

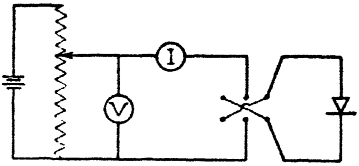
† Phil Mag., July 1928, p. 175.

‡ Palmer, 'Wireless Principles and Practice,' p. 304.

EXPERIMENTAL.

The steady current characteristic of a crystal detector, that is, the curve connecting the current flowing through the crystal contact and the steady applied voltage, enables one to determine whether a given crystal will rectify efficiently and what value of potential, steadily applied, will make the degree of rectification a maximum. The characteristic may be determined by means of the circuit of fig. 1, in which I is a microammeter and V a voltmeter of high resistance compared with that of the contact. The points on the characteristic for which the second differential is a maximum give the points for best rectification.

Fig. 1.



Effect of Ultra-violet Light.

The characteristic curve of the crystal under test was determined before exposure to the ultra-violet light. The source of light was a medical quartz mercury-vapour lamp, without filter, consuming 4 amperes from a 230 volt direct-current supply. The light-spectrum of this lamp covers a wave-length band from 0·43 to 0·23 millimicrons. The output of heat rays is stated to be very low. During exposure the crystal was supported at a distance of one foot from the tube, the rays from which were allowed to play directly upon the crystal contact. A small steady potential was applied to the crystal and the change of current, flowing under the influence of this applied pressure, with time of exposure noted. When the current had reached a steady value, the characteristic curve was redetermined under exposure. Before extinguishing the mercury-vapour lamp, the applied voltage to the crystal was adjusted to the same value as that during exposure, and the change of current observed after the rays had been cut off. A final characteristic curve was determined when the current again reached a steady value.

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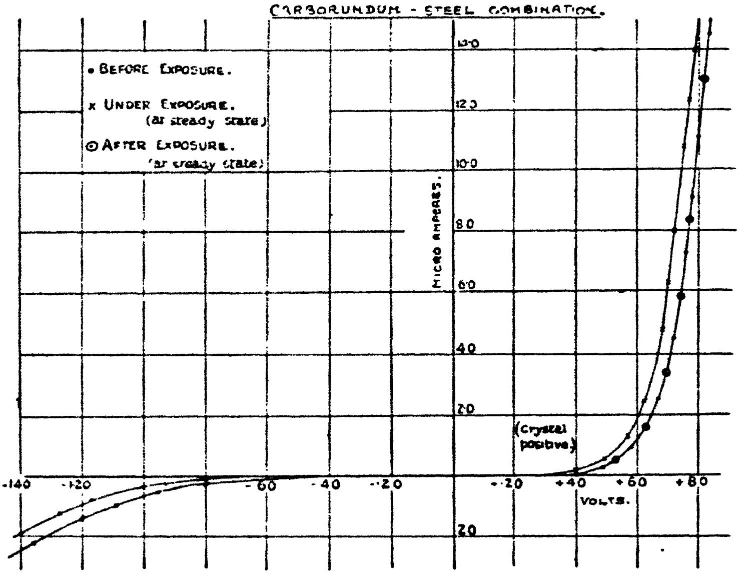
[*] H. Pélabon, *Comptes Rendus*, clxxii. p. 143 (Jan. 11, 1926).

[†] Palmer, 'Wireless Principles and Practice,' p. 303.

Fig. 2.

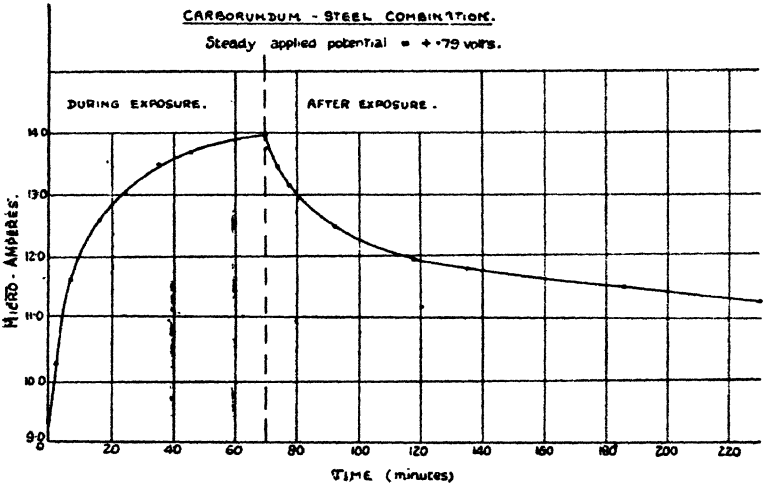


The curves of fig. 2 show the results obtained with a carborundum-steel combination. During exposure there occurred a rise in current, rapid at first, but more slowly as the steady state was approached. The nature of the current change is shown in fig. 3. This increase in conductivity of the crystal contact is seen from fig. 2 to be more pronounced for positive than for negative applied voltages. The steady state under the ultra-violet light was not reached until after an exposure of more than an hour. After extinguishing the arc the fall in current which resulted was very slow, but after a period of several hours the crystal had reached its original state and provided the same characteristic as before exposure.

Similar tests were performed on hertzite, galena, and silicon crystals, using a silver wire as contact-point. Of those tested, the crystal on which the effect of the rays was most pronounced is known by the trade name "Stutzberg." The results with this crystal are given in figs. 4 and 5.

An examination of the characteristic curves of the several crystals tested, taken before and at the steady state during exposure, leads to the conclusion that along with the increased conductivity of the crystal contact under the rays, there occurs a slight decrease in value of the maximum curvature of the characteristic, and with this a reduction in the rectifying properties at the point of best rectification.

Fig. 3.



Effect of X-Rays.

The same procedure as described above was adopted in examining the effect of exposure to X-rays. During exposure the crystal was supported at a distance of 4 inches below the X-ray tube. The quality of the rays used was 8 Benoist. There occurred an increase in current through the crystal with time of exposure, rapid at first and more slowly as the steady state was approached. As the

Fig. 4.

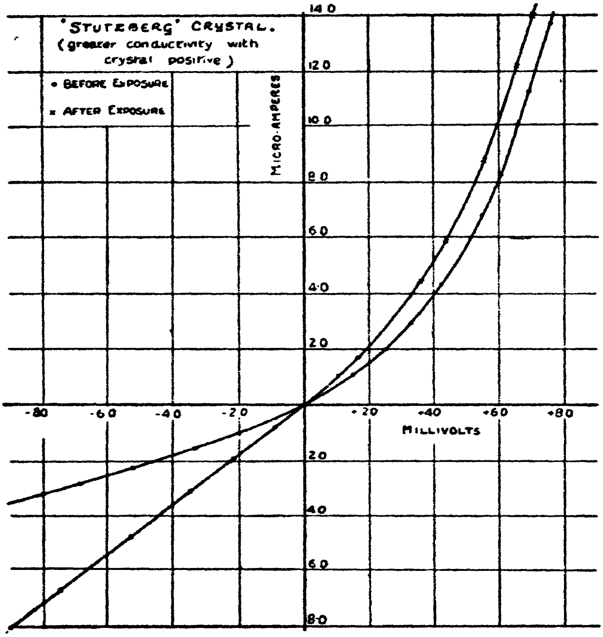
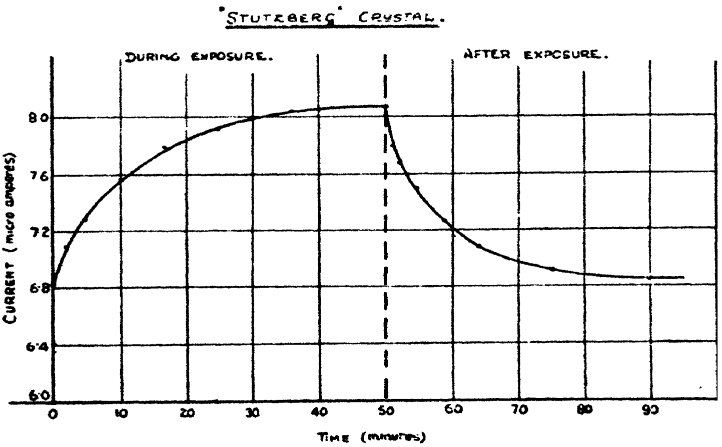

'STUTZBERG' CRYSTAL.
(greater conductivity with crystal positive)
• BEFORE EXPOSURE
× AFTER EXPOSURE
MICRO-AMPERES
14.0
12.0
10.0
8.0
6.0
4.0
2.0
2.0
4.0
6.0
8.0
-80
-60
-40
-20
+20
+40
+60
+80
MILLIVOLTS

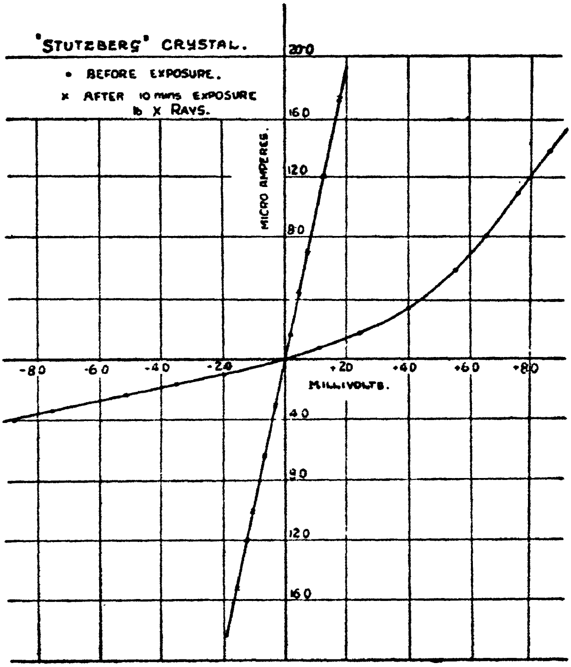
Fig. 5.


'STUTZBERG' CRYSTAL.
DURING EXPOSURE.
AFTER EXPOSURE.
CURRENT (micro amperes)
8.0
7.6
7.2
6.8
6.4
6.0
0
10
20
30
40
50
60
70
80
90
TIME (minutes)

changes in current were not gradual but often took place in jerks, it was not possible satisfactorily to plot a curve showing the nature of the change with time.

In the case of the hertzite, galena, silicon, and "Stutzberg" crystals, the unidirectional and rectifying properties were completely destroyed, and even after several hours of rest there was no indication of a recovery of these properties. Fig. 6 shows the results on the "Stutzberg" crystal, those relating to the other crystals mentioned being essentially similar in nature.

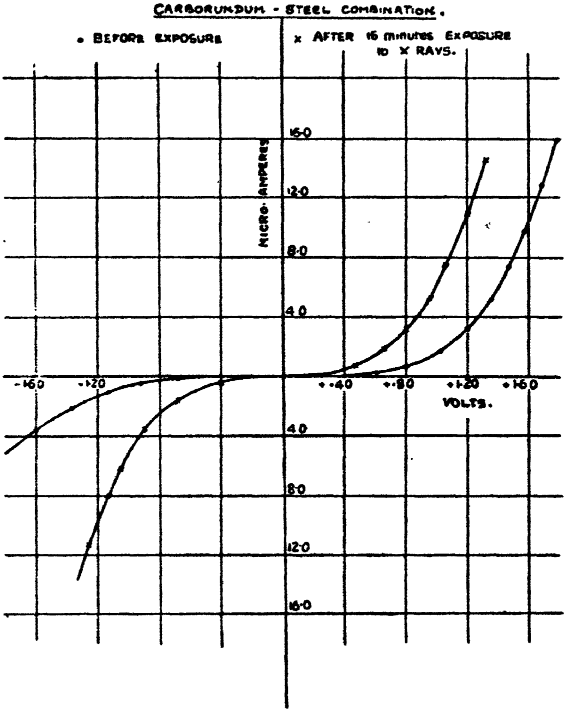
Fig. 6.



With the carborundum-steel combination, the results on which are given in fig. 7, the loss of unidirectional property is noticeable although the rectifying property is retained for both positive and negative values of applied voltage.

It has not been possible to draw any definite conclusions from the results obtained during the short opportunity presented for carrying out the recorded work. Their statement may, however, prove of interest and suggest possibilities for future investigation, which may help to substantiate one or other of the above summarized theories of crystal rectification.

Fig. 7.



The writer's thanks are due to Dr. Williams, School Medical Officer for Bradford, and to Mr. W. H. N. James, of the Technical College, for the facilities provided.

CI. *On the Effect of Constrictions in Kundt's Tube and Allied Problems.—II. Some Theoretical Considerations.* By ERIC J. IRONS, *B.Sc., East London College, E.* 1 *.

1. INTRODUCTION.

IN a previous paper ⁽¹⁾ the results of experiments to determine the effect of introducing diaphragm constrictions on the distribution of nodes and antinodes in a Kundt's sound-tube apparatus were described, and some measurements of the end corrections of a partially-stopped tube were recorded. In the present communication these results are examined by the principles of "acoustical impedance" introduced by Webster⁽²⁾ and, in addition, formulæ giving the proper tones of various simple forms of resonator are derived.

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* Communicated by the Author.

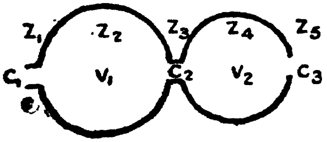
2. THEORETICAL.

According to Stewart⁽³⁾ the impedances of an orifice, reservoir, pipe with a closed end, and pipe with an open end may be taken as

$$\frac{i\rho\omega}{c}, \quad \frac{-i\rho a^2}{\omega V}, \quad \frac{-i\rho a}{S}\cot\frac{\omega L}{a}, \quad \frac{i\rho a}{S}\tan\frac{\omega L}{a} \quad . \quad (1)$$

respectively *, where $i = \sqrt{-1}$, ρ = density of medium, a = velocity of sound, $\omega = 2\pi$ (frequency), V = volume of reservoir, c = conductance of orifice, and S and L are area of cross-section and length of pipe respectively.

Fig. 1.



Terms involving "radiation resistance" and friction are neglected as small compared with the terms retained.

The natural tones of a number of common forms of resonator are easily calculated by the application of the above formulæ, and, as they may be of service as mnemonics, formulæ for some ten forms are tabulated below. This paper is primarily concerned with two of these forms (numbers 5 and 6).

(1) *Rayleigh Double Resonator.* (Fig. 1.)

The resonator consists of two reservoirs of volumes V_1 and V_2, communicating with each other and with the external air by passages having conductances c_2, c_1, and c_3 respectively. Let Z_1, Z_2, Z_3, . . . (fig. 1) represent the impedances of the different elements of the resonator. The medium in V_1 may, when displaced, flow through either of the passages of conductance c_1 or c_2, which must therefore be considered in parallel. Suppose the impedance of Z_3, Z_4, and Z_5 considered as one unit be represented by P, then the combined impedance of Z_1 and P in parallel must be considered in series with Z_2, and for resonance the resultant must be equated to zero. Thus

---

* It may be noted that if the length L of the pipe be so small that $\tan \omega L/a$ may be replaced by $\omega L/a$, then the expression for the impedance of a closed pipe reduces to that of a reservoir, while the value for an open pipe becomes identical with that of an orifice.

$$\frac{PZ_1}{P+Z_1}+Z_2=0.$$

Similarly, considering the motion of the fluid in V_2 and supposing the impedance of Z_1, Z_2, and Z_3 considered as one unit to be P′, we have

$$\frac{P'Z_5}{P'+Z_5}+Z_4=0.$$

Finally, .P and P′ (*both* of which include Z_3) may be considered in series; so that for resonance

$$P+P'-Z_3=0.$$

Eliminating P and P′ from these equations gives

$$\frac{Z_1Z_2}{Z_1+Z_2}+\frac{Z_4Z_5}{Z_4+Z_5}+Z_3=0,$$

and substituting the appropriate values from equation (1), we have

$$\omega^4-a^2\omega^2\left\{\frac{c_1+c_2}{V_1}+\frac{c_2+c_3}{V_2}\right\}+\frac{a^4}{V_1V_2}\left\{c_1c_3+c_2(c_1+c_3)\right\}=0, \quad . \quad . \quad . \quad . \quad (2)$$

which is in agreement with Rayleigh's $^{(4)}$ result obtained by the method of Lagrange *.

(2) *Helmholtz Double Resonator.* (Fig. 2.)

The formula for this type of resonator has been obtained on impedance principles by Richardson$^{(5)}$ and on different grounds by Paris$^{(6)}$. Following Rayleigh, the formula may be obtained directly from equation (2) by putting $c_3=0$, when

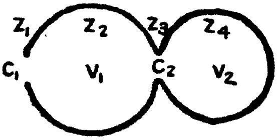
$$\omega^4-a^2\omega^2\left\{\frac{c_1+c_2}{V_1}+\frac{c_2}{V_2}\right\}+\frac{a^4c_1c_2}{V_1V_2}=0, \qquad (3)$$

---

* Rayleigh contemplates the frequency of the natural tones to be given, in his notation, by $n^2=-p^2/4\pi^2$, which accounts for the positive coefficient of p^2 in his equation.

or, following Richardson, by adding Z_3 and Z_4 in series, taking the resultant of these in parallel with Z_1 and equating the series sum of this quantity and Z_2 to zero.

Fig. 2.



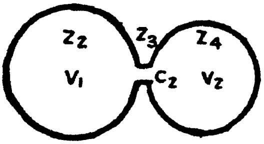
(3) "*Dumb-bell*" *Resonator.* (Fig. 3.)

From first principles, $Z_2+Z_3+Z_4=0$ for resonance, and, substituting the appropriate values from equation (1), we have

$$\omega^2-a^2c_2\left(\frac{1}{V_1}+\frac{1}{V_2}\right)=0, \quad . \quad . \quad . \quad . \quad (4)$$

which agrees with the result obtained from equation (3) by putting $c_1=0$.

Fig. 3.



(4) *Reservoir with two (or more) openings.*

In equation (2) put $V_2=\infty$ and

$$\omega^2-a_2\left(\frac{c_1+c_2}{V_1}\right)=0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

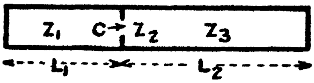
or, from first principles, add the impedances of the openings in parallel, and, to the result, add the impedance of the reservoir and equate to zero for resonance. (See (4).)

(5) *Constrictions in Kundt's Tube.* (Fig. 4.)

If the reservoirs of (3) be replaced by closed pipes, and the passage of conductance c_2 by a diaphragm pierced by a circular hole, we have, for resonance, substituting the impedance of a closed pipe for that of a reservoir, or, alternatively, substituting the appropriate values in the equation $Z_1+Z_2+Z_3=0$,

$$\frac{\omega}{c}=\frac{a}{S}\left(\cot\frac{\omega L_1}{a}+\cot\frac{\omega L_2}{a}\right). \quad . \quad . \quad . \quad . \quad (6)$$

Fig. 4.



(6) *Partially-stopped Pipe, or Helmholtz Resonator of Cylindrical Form.*

If one of the pipes, say L_2, of (5) is removed, we are left with a partially-stopped pipe or Helmholtz resonator, for the natural frequencies of which

$$\frac{i\rho\omega}{c}-\frac{i\rho a}{S}\cot\frac{\omega L}{a}=0$$

or

$$\tan\frac{\omega L}{a}=\frac{ac}{\omega S}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

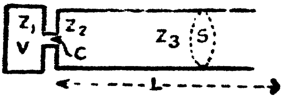
an equation deduced on these lines by Richardson (*loc. cit.*) and previously given by Rayleigh (*loc. cit.*).

(7) *Boys Resonator.* (Fig. 5.)

This consists of a pipe open at one end and having an orifice leading to a resonator at the other end. Let the quantities involved be as shown in fig. 5, L being the length of the pipe including the end correction, so that for resonance $Z_1+Z_2+Z_3=0$, or, in terms of equation (1),

$$\frac{i\rho\omega}{c}-\frac{i\rho a^2}{\omega V}+\frac{i\rho a}{S}\tan\frac{\omega L}{a}=0,$$

Fig. 5.



which, writing the frequency of the resonator with orifice when separated from the rest of the system as $n_1\left(=\frac{a}{2\pi}\sqrt{\frac{c}{V}}\right)$, gives

$$\tan\frac{\omega L}{a} = -\frac{2\pi S}{ac}n_1\left(\frac{n}{n_1}-\frac{n_1}{n}\right), \quad . \quad . \quad . \quad (8)$$

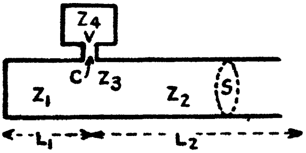
which is the result obtained by Paris(6).

(8) *Stopped Pipe with Helmholtz Resonator on the side.* (Fig. 6.)

The medium in the pipe of impedance Z_2 may, when displaced, move either into the pipe of impedance Z_1 or through the orifice into the resonator. It follows that Z_1 and (Z_3+Z_4) must be added in parallel, the result increased by Z_2, and the whole be equated to zero for resonance. Thus

$$Z_2+\frac{Z_1(Z_3+Z_4)}{Z_1+Z_3+Z_4}=0,$$

Fig. 6.



which, after some reduction, gives, on substituting the appropriate values from equation (1),

$$-\frac{2\pi S}{ac}.n_1\left(\frac{n}{n_1}-\frac{n_1}{n}\right)=\frac{1}{\cot\frac{\omega L_2}{a}-\tan\frac{\omega L_1}{a}}$$

$$=\frac{1}{\cot kl'-\tan k(L'-l')} \quad (9)$$

in the nomenclature of Paris (*loc. cit.*).

(9) "*Bottle-pipe*" *Resonator.*

Aldis(7) has given a formula for the natural tones of a resonator of the form of fig. 7: it is readily obtained by adding the impedances of an open pipe and a closed pipe in series, when

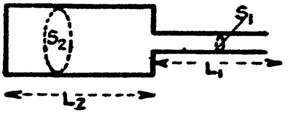
$$-\frac{ipa}{S_2}\cot\frac{\omega L_2}{a}+\frac{ipa}{S_1}.\tan\frac{\omega L_1}{a}=0$$

or

$$\tan\frac{\omega L_1}{a}.\tan\frac{\omega L_2}{a}=\frac{S_1}{S_2}. \quad . \quad . \quad . \quad (10)$$

Paris ⁽⁸⁾ has pointed out that this formula embodies Rayleigh's formulæ for the natural tones of a Helmholtz resonator, a stopped pipe with restricted mouth, and a long tube connected with a reservoir of small volume.

Fig. 7.



(10) *Rohrflöte.*

Benton ⁽⁹⁾ has drawn attention to the Rohrflöte pipe, in which the "stopped" end is fitted with an open chimney. In this instance the impedances of two open pipes must be added in series, when

$$\tan\frac{\omega L_1}{a}\Big/\tan\frac{\omega L_2}{a} = -r^2/R_2 \quad . \quad . \quad . \quad (11)$$

(r and R being the radii of the lengths L_1 and L_2 of the chimney and pipe respectively), which is the result given by Benton.

3. EXAMINATION OF PREVIOUS EXPERIMENTAL WORK IN THE LIGHT OF THE ABOVE THEORY.

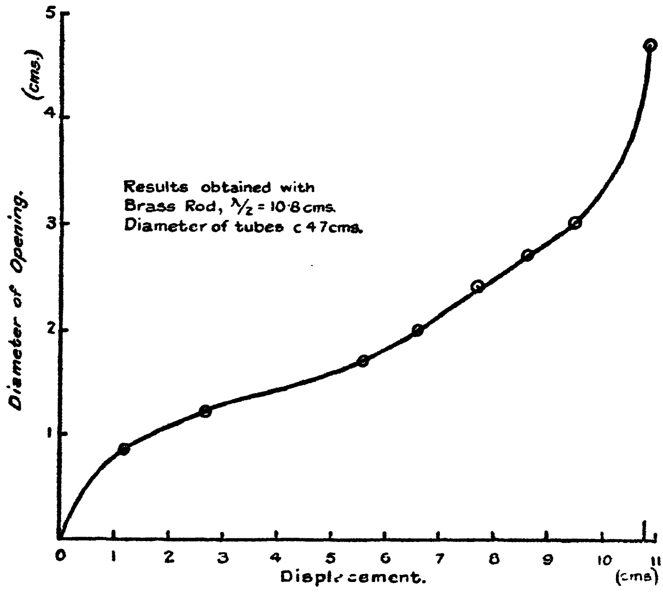
Part I. *Experiments with Constrictions.*

Full details of the experimental work are given in the paper cited ⁽¹⁾. It will suffice here to state that a diaphragm was placed between two glass tubes one of which was fitted with a movable stopper, while into the other the end of a rod, suitably clamped and fitted to serve as a source of sound, was allowed to protrude—the whole forming a "Kundt's tube with constriction."

Two types of experiment were carried out. In the first the mode of production of *good dust figures* was investigated. The results occurred in two groups, in both of which the antinodes in the two tubes were found to be symmetrically placed with respect to the constriction. In Group A no displacement of the antinodes was found, *i. e.*, the constriction appeared to form a node whatever the area of the opening in the constriction; while in Group B the antinodes were moved out from the constriction in both tubes to an extent shown in fig. 3 of the experimental paper.

Although the positions of the antinodes were measured and recorded it will be more convenient here to deal with the positions of the nodes, spaced midway between the antinodes in each tube, and to redefine the "Displacement" as the distance between the *nodes* nearest to the constriction in each tube. Thus, when the constriction is entirely closed (nodes coinciding with constriction in both tubes), the displacement will be zero; and when the constriction is "open" (and, according to results of Group B, an antinode may be considered as situated at it) the displacement will be a quarter wave-length in respect to each tube, and therefore

Fig. 8.



half a wave-length in all. The experimental results are shown in fig. 8, which is a graph of displacement against the diameter of opening in the constriction for a half wave-length of 10·8 cm.

In what follows it will be necessary to neglect energy losses due to reflexion and to friction so that the nodes may be considered as planes of no motion and, theoretically, may be replaced by solid walls.

Equation (6)—

$$\omega = \frac{ac}{S}\left(\cot\frac{\omega}{a}L_1 + \cot\frac{\omega}{a}L_2\right)$$

(where L_1 and L_2 represent the distances between the constriction and the nearest nodes in each tube)—may then be applied to the system. For results of Group B, $L_1 = L_2 =$ half of the displacement D, as defined above, whence

$$c = \frac{\omega S}{2a} \tan\frac{\omega}{a} \cdot \frac{D}{2}$$

$$= \frac{\pi S}{\lambda} \tan\frac{\pi}{\lambda/2} \cdot \frac{D}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

substituting for ω in terms of the wave-length λ, which was 21·6 cm.

By substituting the Group B data for this wave-length in equation (12), the following table of conductances has been prepared for the openings of the various constrictions placed in a tube of cross-sectional area of 17·3 sq. cm.

Diameter of orifice :	·84,	1·2,	1·7,	2·0,	2·4,	2·7,	3·0 cm.
Conductance :	·44,	1·0,	2·7,	3·6,	5·2,	7·6,	13·2 cm.

The second type of experiment was concerned with tracing, with any one constriction, *the positions of the antinodes (or nodes) corresponding to given positions of the stopper*, and the results obtained in a particular instance are indicated in fig. 4 of the experimental paper (1). Under these conditions equation (6) will take the form :

$$\cot \pi\frac{L_1}{\lambda/2} + \cot\pi\frac{L_2}{\lambda/2} = \frac{2\pi S}{\lambda c} = K \text{ (a constant).} \qquad (13)$$

This equation has been tested for the instance quoted by assigning values to L_2 and, using the value of c determined by equation (12) *, calculating the corresponding values of L_1. Fig. 9 is a reproduction of fig. 4 of the experimental paper (1), and shows the agreement between experiment and theory.

In general it is convenient to discuss equation (13) graphically by means of the following construction (fig. 10). On XY set off a length AB=K. Parallel to, and at unit distance from XY draw another line MN. At A set off

$$\widehat{BAC} = \frac{\pi L_1}{\lambda/2},$$

cutting MN in C. Join CB. From C draw a perpendicular to XY meeting it in D.

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* This is tantamount to fixing one point on the L_1 curve.

Fig. 9.

⊙ Positions of Antinodes } Determined by experiment.
↓ „ „ Nodes }
↑ Calculated positions of Nodes.
1 Indicates point an integral number of half wave-lengths from stop.

Symmetry corresponding to :—

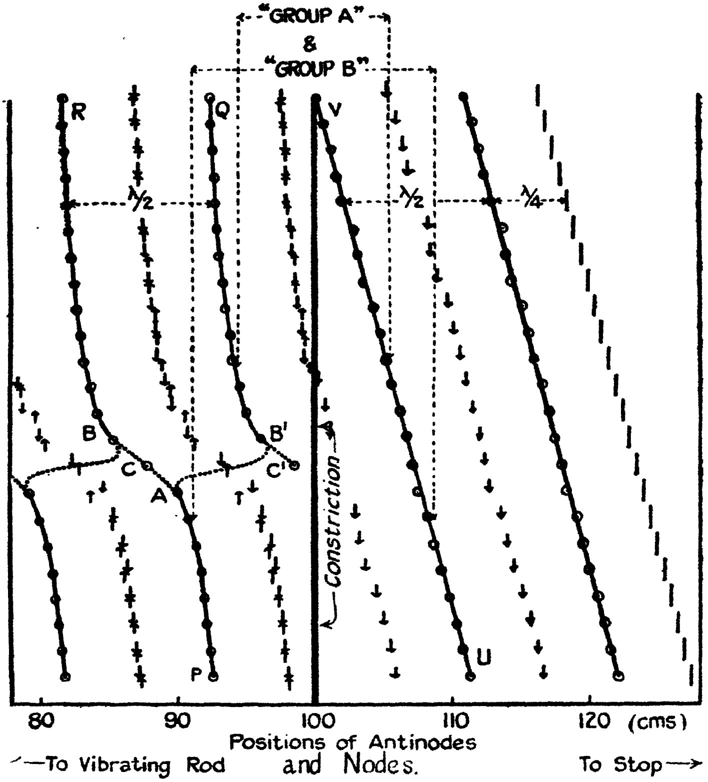
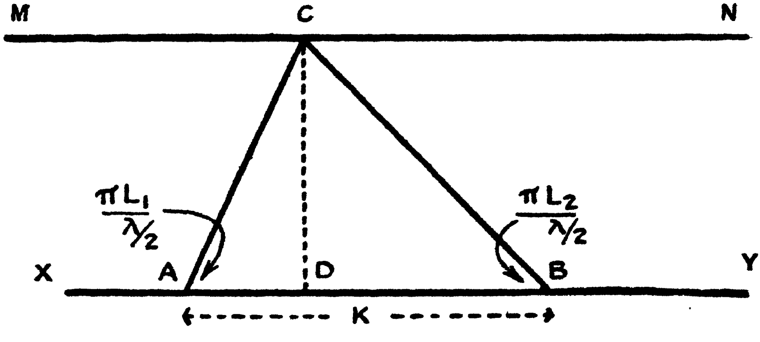


Fig. 10.



Then $\quad AD=\cot\frac{\pi L_1}{\lambda/2},\quad AB=K,$

so $\quad DB=\cot\frac{\pi L_2}{\lambda/2}\quad$ and $\quad \widehat{CBD}=\frac{\pi L_2}{\lambda/2}.$

Hence, if K be known, the value of L_2 corresponding to any value of L_1 (or *vice versâ*) may be obtained from the figure.

Three notes are appended which show the general agreement between the facts observed and recorded in the experimental paper (1) and deductions from the above construction based on theory:—

(*a*) If the opening in the constriction be large, *c* is large, K is correspondingly small, and $\widehat{ACB}$ is small so that

$$\frac{\pi L_1}{\lambda/2}+\frac{\pi L_2}{\lambda/2}=\pi-\widehat{ACB}=\pi \text{ (approx.) and } L_1+L_2=\lambda/2\ ;$$

i.e., the effect of the constriction is small and nodes (or antinodes) in both tubes are in step in spite of the presence of the constriction.

(*b*) If the opening in the constriction be small, *c* is small and K is correspondingly large. It follows that $\widehat{ACB}$ will usually be large and $\frac{\pi(L_1+L_2)}{\lambda/2}$ small; *i.e.*, L_1 and L_2 will both be small and the nodes will be near the constriction in both tubes.

(*c*) $L_1=L_2$ when

(i.) $\widehat{CAB}=\widehat{CBA}$ corresponding to Group B results,

and (ii.) when $\frac{\pi L_1}{\lambda/2}=\pi$, $\frac{\pi L_2}{\lambda/2}=0$, and *vice versâ*; *i.e.* $L_1=L_2=0$ or $\lambda/2$, or the nodes coincide with the constriction as in Group A results.

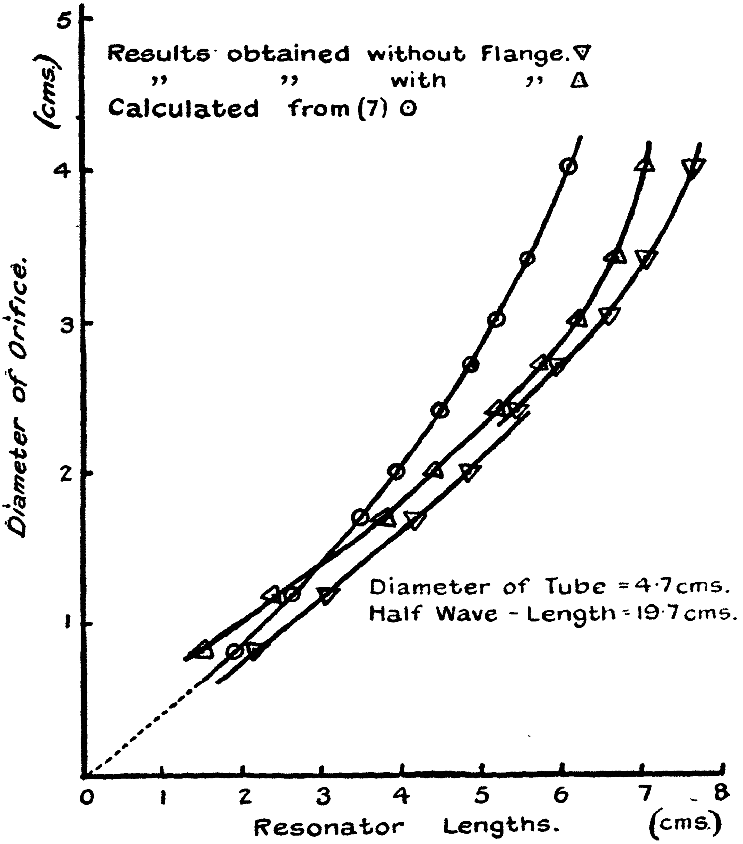
Part II. *Experiments with Caps.*

We pass finally to the consideration of equation (7) in the light of results obtained by placing caps, having orifices of various diameters, on the end of a single Kundt's tube. The discussion will be restricted to the results shown in fig. 7 of the experimental paper (1), as they correspond to the largest half wave-length (19·7 cm.) and are therefore most in accordance with the postulates of theory. For convenience these results have been replotted (fig. 11) with L (the distance of the nearest node from the cap or the "length" of the resonator $\{=\lambda/4-\text{end correction}\}$) as abscissa, and the diameter of the orifice in the cap as ordinate.

As Richardson (*loc. cit.*) has pointed out, equation (7),

$$\tan\frac{\omega L}{a}=\frac{ac}{\omega S} \quad \text{or} \quad \tan\frac{\pi L}{\lambda/2}=\frac{\lambda}{2\pi}\cdot\frac{c}{S},$$

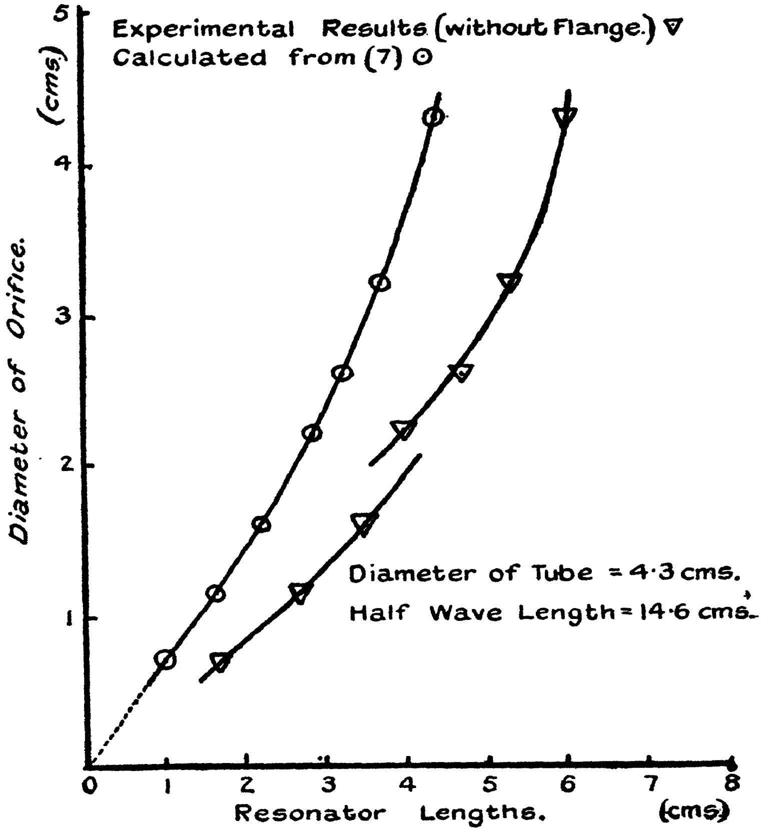
Fig. 11.



embraces both the "resonator" and the "pipe" formulæ. Assuming c, the conductance of the orifice, to be equal to the diameter of the orifice, the values of L calculated from equation (7) may be compared with those observed by reference to fig. 11 of this paper. Richardson's observed values (obtained by the Blaikley method), together with those calculated from equation (7) in the instance most similar as regards wave-length and diameter of tube to the one under consideration, have been graphed on the same scale for comparison (fig. 12).

It will be seen that the discontinuity observed by the present author for an unflanged pipe occurs on Richardson's curve; it may also be observed in the other results he quotes.

Fig. 12.



Equation (7) furnishes a justification for two empirical rules given in the former communication (1).

First, if c is small, then $\tan\frac{\omega L}{a}$ is small, and may be replaced by $\frac{\omega L}{a}$, so that

$$\omega = a\sqrt{\frac{c}{L.S}} = a\sqrt{\frac{2r}{L.S}},$$

where r is the radius of the opening in the cap. Hence, S and ω being constant, $(r/\mathrm{L})^{\frac{1}{2}}$ should be constant as previously explained ⁽¹⁾.

Second, if in equation (7) we denote end correction by e and write for L, $(\lambda/4-e)$, then

$$\tan\frac{\pi \mathrm{L}}{\lambda/2}=\tan\frac{\pi(\lambda/4-e)}{\lambda/2}=\cot\frac{\pi e}{\lambda/2}=\frac{\lambda\,.\,c}{2\pi\,.\,\mathrm{S}}$$

or
$$c\tan\frac{\pi e}{\lambda/2}=\frac{2\pi\mathrm{S}}{\lambda}.$$

Further, for flanged caps with openings between 1 and 2 cm. radius and a half wave-length of 19·7 cm., we have approximately $2{\cdot}5<e<5{\cdot}0$, *i. e.*, $\frac{\pi}{8}<\frac{\pi e}{\lambda/2}<\frac{\pi}{4}$ and, very roughly, we may replace the tangent over this range by 1·2 times the angle so that

$$c\,.\,1{\cdot}2\,.\,\frac{\pi e}{\lambda/2}=\frac{2\pi\mathrm{S}}{\lambda}$$

or
$$c\,.\,e=\frac{\mathrm{S}}{1{\cdot}2}=\frac{17{\cdot}1}{1{\cdot}2}=14{\cdot}3,$$

inserting the value of the cross-sectional area of the tube. Now, by experiment it was found that

$$r\,.\,e=5{\cdot}5 \quad\text{or}\quad (2r)\,.\,e=11{\cdot}0,$$

where r was the radius of the hole in the cap. Rayleigh (*loc. cit.*) has suggested that the conductance of an orifice is equal to its diameter, but, to reconcile theory with practice, the conductances of the orifices in question must be assumed to be somewhat greater than their diameters, and this might reasonably be expected, considering that the radius of the tube was only about 2·5 cm.

References.

(1) Irons, Phil. Mag. v. p. 580 (1928).

(2) Webster, Proc. Nat. Acad. Sci. v. p. 275 (1919).

(3) Stewart, Phys. Rev. xx. p. 528 (1922) *et sqq.*

(4) Rayleigh, Phil. Trans. clxi. p. 77 (1870), or Scient. Papers, i. p. 33 (1899).

(5) Richardson, Proc. Phys. Soc. xl. p. 206 (1928).

(6) Paris, Proc. Roy. Soc. A, ci. p. 391 (1922); Phil. Mag. xlviii. p. 769 (1924).

(7) Aldis, 'Nature' cxiv. p. 309 (1924).

(8) Paris, *ibid.* p. 465 (1924).

(9) Benton, *ibid.* p. 573 (1924).

CII. *Coefficient of Cubical Expansion of Liquids and Critical Temperature.* *By* V. N. THATTE, *M.Sc.(Allahabad)* *.

IN the Phil. Mag. for April 1912 Mr. Davies gives a relation between the coefficient of cubical expansion of a liquid and its critical temperature. The relation is based on Mathias's law of rectilinear diameters and Guldberg's calculation of the ratio of densities of a liquid at 0° C. and at the critical temperature.

Mr. Davies finds that the relation

$$C=\frac{1}{v}\left(\frac{dv}{dT}\right)_p=\frac{1}{2T_c-T}$$

is true for a number of liquids, where C is the coefficient of expansion of a liquid, T_c is the critical temperature on the absolute scale, and T is the absolute temperature at which the coefficient of expansion is measured.

The object of the present paper is to seek a similar relation from an equation of state of the type of van der Waals's equation.

Writing van der Waals's equation in the form

$$p+\frac{a}{v^2}=\frac{RT}{(v-b)}, \quad \ldots \ldots \quad (1)$$

we have by differentiation at constant pressure

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p\left[-\frac{2a}{v^2}+\frac{RT\,.\,v}{(v-b)^2}\right]=\frac{R}{(v-b)}. \quad \ldots \quad (2)$$

If this equation is applicable to the liquid state, the term $\frac{a}{v^2}$, which is the internal molecular pressure (intrinsic pressure of Laplace), is very large compared with the external pressure p, and hence

$$\frac{a}{v^2}\doteq\frac{RT}{v-b}. \quad \ldots \ldots \quad (3)$$

Making this substitution in (2), we readily find

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p=\frac{1}{\frac{a}{vR}-2T}. \quad \ldots \ldots \quad (4)$$

The quantity $\frac{1}{R}$ is proportional to T_c, the critical temperature of the liquid, and, assuming that the ratio of the actual volume of the liquid occupied by the molecules to the total volume of the liquid is practically constant for liquids under ordinary conditions of temperature and pressure, equation (4) takes the form

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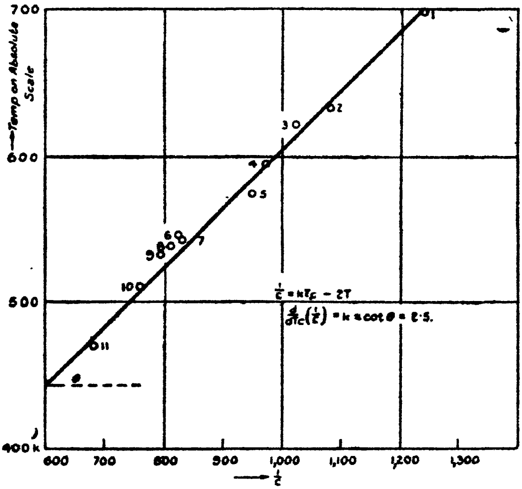
* Communicated by Prof. Alfred W. Porter, F.R.S.

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p = \frac{1}{kT_c - 2T}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If C denotes the coefficient of cubical expansion,

$$\frac{1}{C} = kT_c - 2T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

To determine the numerical value of the constant k, a graph was drawn connecting $\frac{1}{C}$ with T_c for different liquids, as shown on the accompanying diagram; and the best straight line was drawn through the several points.



1. Aniline.
2. Xylol.
3. Amyl alcohol.
4. Toluol.
5. Bromine.
6. Carbon bisulphide.
7. Amyl alcohol.
8. Propyl alcohol.
9. Chloroform.
10. Acetone.
11. Pentane.

The graph shows that a linear relation of the type (6) represents with considerable accuracy the relation between the coefficients of expansion and critical temperature for liquids.

As indicated by the slope of the straight line, the numerical value of the constant k was taken to be 2·5; and equation (6), written in the following form, was used to calculate the coefficient of expansion of liquids from known values of the critical temperature :

$$C=\frac{1}{kT_c-2T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

The constants used in Table I. were taken from Landolt and Börnstein's tables and Kaye and Laby's tables.

In the case of substances which are solid at 0° C., C is calculated at the lowest temperature at which these substances are in the liquid state.

TABLE I.

Liquid.	Critical temp. in ° C.	$C=\frac{1}{2{\cdot}5\,T_c-2T}$.	Experimental values of C.	Davies's formula, $C=\frac{1}{2T_c-T}$;
Pentane	197	·00155	·001464 ·0016	·001499
Ethyl alcohol ...	247	·00131	·00110	
Methyl alcohol ...	232 240	·00135	·00134	
Propyl alcohol ...	265	·00122	·00119	·00124
Allyl alcohol ...	271·9	·00119	·00113	
CS_2	273	·00119	·00121	
Toluol	321	·00105	·001028	·001062
Chloroform	260	·00124	·00126	
Bromine...........	302	·00110	·00104 ·001103	·001167
Aniline	426	·000817	·00082	·000869
Xylol	358	·00099	·001016	·00101
Acetone	237	·00133	·001324	·001339
Amyl Alcohol ...	348	·00097	·00094	·00103

For purposes of comparison the values of C as given by Davies's formula are also shown in the table.

In calculating the value of C from equation (6), the integer nearest the known value of critical temperature has been used, and also where the tables gave values of critical temperature by different observers the mean value was used in the calculation.

From the agreement between the calculated values and observed values of coefficient of expansion, it would appear that the process of calculation could be reversed, and the equation (6) could be used for calculating the critical temperature if the coefficient of expansion is known. It is assumed throughout that the coefficient is for a temperature remote from the critical value.

Relations similar to that expressed by equation (6) could be obtained by using Clausius's or Dieterici's equation of state.

It is also interesting to see how the equation (7) holds for liquefied gases, the pressure being sufficiently moderate, so that the assumption

$$\frac{a}{v^2} \bumpeq \frac{RT}{(v-b)}$$

in the derivation of equation (7) is valid.

TABLE II.

Coefficients of Expansion of Liquefied Gases.

Critical temp. in ° C.	Critical press. in atmospheres.	Liquefied gas in ° C.	C given by equation (7).	Experimental values of C.	Davies's formula, $C=\frac{1}{2T_c-T}$.
130	115	Ammonia −50 to 0	·00195	·00193 *	·00179
154·7	78·9	Sulphur dioxide - 50 to 0	·00174	·00170 *	·0015
31·1	73	Carbon dioxide −50 to 0	·00476	·00495 *	·00279
−118	50	Oxygen near −200	·00416	·00385 †	·00427
−146	33	Nitrogen near −200	·0058	·00558 †	·0052
−141	35·9	Carbon monoxide near −200	·0058	·00491 †	·0052
−117·4	52·9	Argon near −200	·0044	·00451 †	·0043
146	93·5	Chlorine			
		−102 to −23	·00150	·001409 ‡	·00150
		- 30 to 0	·00178	·001793 ‡	·0016
		0 to 10	·00193	·001958 ‡	·0018

* Lange. † Baly and Donnan. ‡ Knietch.

The experimental data shown in Table II. are taken from Landolt and Börnstein's tables. In the case of chlorine (liquid state) the coefficient of expansion increases with temperature. This is also shown by the calculated values from equation (7) and those from Davies's formulæ.

Table III. shows the pressures of some of the liquefied gases at various low temperatures, showing how far the assumption

$$\frac{a}{v^2} \bumpeq \frac{RT}{(v-b)}$$

is valid in these cases.

TABLE III.

Liquefied gases.	Temperature ° C.	Pressure in atmospheres.	Observer.
Liquid CO_2 ...	−54	5·46	Cailletet.
	−54	4·6	
	−45	8·88	Faraday.
Liquid SO_2 ...	−10	1	Regnault.
	− 3·3	1·33	Faraday.
Liquid NH_3 ...	−30	1·14	Pictet.
	−15	2·28	

The external pressure p is only a few atmospheres as compared with the intrinsic pressure $\frac{a}{v^2}$, which in the case of liquids is of the order of thousands of atmospheres.

CIII. *The Refractivity of Gaseous Compounds.* *By* G. W. BRINDLEY, *M.Sc., Demonstrator in Physics, University of Leeds* [*].

1. *Introduction.*

IN a recent note to 'Nature' [†], attention has been drawn to some simple relations which appear to exist between the refractivities of a number of gaseous compounds which, so far as the writer knows, have not been published elsewhere. The aim of the present paper is to discuss these relations and to consider how far similar arguments may be applied to other gaseous compounds.

2. *Survey of Previous Work.*

It has been generally observed [‡] that the refractivities of simple gaseous compounds do not follow an additive rule. Fajans and Joos [§], using data obtained from the refractivities of solids, liquids, solutions, and gases, have shown that as the nuclear charge increases in a series such as O^{--}, F^{-}, Ne, Na^{+}, Mg^{++}, and Al^{+++}, where each member contains the same number of electrons, the refractivity decreases as the tightness of binding of the electrons increases. They consider that the refractivity of an atom or molecule depends mainly on the outer loosely-bound electrons, and that when combination occurs between atoms the conditoins governing the outer electrons are so much changed that an additive law does not hold. Born and Heisenberg[*] state that in hydrogen chloride the hydrogen nucleus penetrates into the electron shell surrounding the chlorine nucleus, thereby affecting the tightness of binding of the electrons in the chlorine ion, with the result that the refractivity of hydrogen chloride cannot easily be calculated.

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[*] Communicated by Prof. R. Whiddington, F.R.S.

[†] G. W. Brindley, 'Nature,' cxxiii. p. 165 (1929).

[‡] In particular, Cuthbertson in a series of papers in the Proceedings and Transactions of the Royal Society, 1905–1914, in which accurate measurements of many gaseous refractivities are described, has considered the deviations from an additive law. Full references to Cuthbertson's work will be found in Proc. Roy. Soc. A, xcvii. p. 152 (1920).

[§] *Zeit. f. Physik*, xxiii. p. 1 (1924).

Havelock[†] has treated the problem differently by using data derived from the intensity of light scattered transversely by a gas, and has calculated the refractivities of molecules containing two, three, four, and five atoms. In the case of hydrogen chloride, however, the calculated value of the molecular refractivity is 6·267 and the experimental value is 6·695 ; in the case of other gases the agreement is not any closer. For hydrogen chloride, Havelock concludes that "the difference . . . is a measure of the interaction of the two units," that is to say, of H^{+} and Cl^{-}.

So far, therefore, emphasis has been laid on the difference between calculated and observed values.

3. *Relations between Refractivities of some Gaseous Compounds.*

In Tables I., II., III., and IV., a number of simple relations are shown to hold fairly accurately between the refractivities of some simple gaseous compounds for a series of wave-lengths, λ. R(X) denotes values of $(\mu-1)$ for the substance X (corrected, as explained below), μ being the refractive index. It is usual to define the refractivity of a substance as $(\mu^2-1)/(\mu^2+2)$ for theoretical reasons, but for gases, where $(\mu-1)$ is small compared with unity,

$$\left(\frac{\mu^2-1}{\mu^2+2}\right) \doteqdot \tfrac{2}{3}(\mu-1).$$

Hence, in *comparing* refractivities it is justifiable to use $\mu-1)$ as a measure of the refractivity.

It is important to observe that for all the compounds considered the experimental values of the refractivities have been reduced to the values they would have had if the number of molecules per cubic centimetre of the gas or vapour had been equal to the number of molecules per cubic centimetre of hydrogen at 0° C. and 760 mm. pressure. Cuthbertson † has pointed out the convenience of expressing the experimental results in this way in preference to the older method in which they were reduced to 0° C. and 760 mm. pressure, because it enables the refractivities of different gases to be compared directly. The legitimacy of this method depends on the refractivity being proportional to the density and, for a given density, being independent of the temperature.

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[*] *Zeit. f. Physik*, xxiii. p. 388 (1924).

[†] Phil. Mag. iii. pp. 158, 433 (1927).

TABLE I.

$R(HCl) = \frac{4}{7} R(Cl_2)$.

λ.	R . 10^8.			Percentage difference between (2) and (3).
	(1) $R(Cl_2)$.	(2) $R(HCl)$.	(3) $\frac{4}{7}R(Cl_2)$.	
6707·8	77563	44375	44320	−0·1
6438·5	77703	44444	44400	
5790·5	78121	44656	44640	
5769·5	78135	44666	44648	
5460·7	78400	44800	44800	0
5209·1	78651	44930	44944	
5085·8	78791	45007	45024	
4799·9	79166	45187	45240	+0·1

Values of $R(Cl_2)$ and $R(HCl)$ obtained by C. and M. Cuthbertson, Phil. Trans. Roy. Soc. A, ccxiii. p. 1 (1914).

TABLE II.

$R(CCl_4) = \frac{16}{7} R(Cl_2)$.

λ.	R . 10^6.			Percentage difference between (2) and (3).
	(1) $R(Cl_2)$.	(2) $R(CCl_4)$.	(3) $\frac{16}{7}R(Cl_2)$.	
6708	775·63	1774	1772	−0·1
6438	777·03	1778	1776	
6104	779·02*	1782	1780	
5770	781·35	1791	1785	−0·3
5461	784·00	1799	1792	
5086	787·91	1810	1801	
4800	791·66	1819	1809	−0·5

Values of $R(CCl_4)$ obtained by H. Lowery, Proc. Lond. Phys. Soc. xxxix p. 421 (1927).

* Graphical interpolation.

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† Proc. Roy. Soc. A, xcvii. p. 152 (1920); Phil. Trans. Roy. Soc. A, cciv. p. 323 (1905).

TABLE III.

$R(HBr)$ and $R(Br_2)$.

λ.	R . 10⁶. (1) $R(Br_2)$.	 (2) $R(HBr)$.	 (3) $\frac{13}{25}R(Br_2)$.	 (4) $\frac{4}{7}R(Br_2)$.	Percentage difference between (2) and (3)	 (2) and (4).
6708	1152·5	607·5	599·2	658·3	−1·4	+ 7·7
6000	1166·2	611·1*	606·5	666·5	−0·8	+ 9·0
5800	1173·5	612·4*	609·5	670·0	−0·5	+ 9·4
5461	1184·9	614·9	616·0	677·0	+0·2	+10·1

Values of $R(Br_2)$ and $R(HBr)$ obtained by C. and M. Cuthbertson, *loc. cit.*

* These values obtained by graphical interpolation.

TABLE IV.

$R(CS_2)=\frac{4}{3}R(S_2)$.

λ.	R . 10⁶. (1) $R(S_2)$.	 (2) $R(CS_2)$.	 (3) $\frac{4}{3}R(S_2)$.	Percentage difference between (2) and (3).
6438	1099·3*	1443	1465	+1·54
5770	1113·2*	1464	1484	+1·36
5461	1120·5	1476	1494	+1·21
5086	1132·5	1495	1510	+1·00

Experimental values of $R(S_2)$ were obtained by C. and M. Cuthbertson, Proc. Roy. Soc. A, lxxxiii. pp. 167, 168 (1909), and lxxx. p. 411 (1908); and of $R(CS_2)$ by H. Lowery, Proc. Lond. Phys. Soc. xxxviii. p. 470 (1926).

* Graphical interpolations.

4. *Discussion of Relations between Refractivities.*

In Tables I. and II. the relations between $R(Cl_2)$, $R(HCl)$, and $R(CCl_4)$ hold very closely indeed. In Table IV. the relation between $R(S_2)$ and $R(CS_2)$ does not hold so closely as the previous relations, but it is good compared with the kind of agreement previously obtained between calculated and observed values. The results given in Table III. are discussed in detail below.

The following relations form the basis of a tentative explanation of these results :—

$$(1)\quad \frac{R(HCl)}{R(Cl_2)}=\frac{4}{7}=\frac{\text{Number of M electrons in } Cl^- \text{ ion}}{\text{Number of M electrons in } Cl_2},$$

$$(2)\quad \frac{R(CCl_4)}{R(Cl_2)} = \frac{16}{7} = \frac{4 \times (\text{Number of M electrons in } Cl^{-} \text{ ion})}{\text{Number of M electrons in } Cl_2},$$

$$(2\,a)\quad \text{From (1) and (2)}\ \frac{R(CCl_4)}{R(HCl)} = 4,$$

$$(3)\quad \frac{R(CS_2)}{R(S_2)} = \frac{4}{3} = \frac{2 \times (\text{Number of M electrons in } S^{--} \text{ ion})}{\text{Number of M electrons in } S_2}.$$

In HCl the electron contributed to the molecule by the hydrogen atom completes an argon-like arrangement of electrons round the chlorine nucleus. Assuming that the hydrogen nucleus makes no contribution to the refractivity of HCl, that the K and L electrons are so tightly bound that their contributions to the refractivities of HCl and Cl_2 are small, and that the refractivities arise mainly from the loosely bound M electrons, then relation (1) follows, provided the binding of the M electrons is approximately the same in both molecules. Similarly, in the case of CCl_4 and also of CS_2, assuming the four outer electrons of the carbon atom, which are very loosely-bound, complete argon-like arrangements of electrons round the chlorine and sulphur nuclei, and that the binding of the M electrons in CCl_4 and CS_2 is approximately the same as in Cl_2 and S_2 *, then relations (2), (2 *a*), and (3) follow directly.

These results may be discussed on the basis of the quantum theory of dispersion developed by H. A. Kramers and W. Heisenberg †, according to which

$$\frac{\mu^2-1}{\mu^2+2} = \frac{4\pi}{3} \cdot \frac{Ne^2}{m} \left\{ \sum_{j>k} \frac{f_a}{\omega_{jk}^2 - \omega^2} - \sum_{j<k} \frac{f_e}{\omega_{jk}^2 - \omega^2} \right\}, \quad (1)$$

where the summations extend over possible transitions of electrons ; f_a is proportional to the probability of a transition due to absorption of energy, and f_e due to emission of energy. If the atom is in the ground state, f_e is zero. f_a is greatest for the outermost electrons which are most loosely bound. Hence, if in two different molecules the outer electrons are in similar energy and quantum states the value of f_a for such electrons will be proportional to their number, so that if these conditions are satisfied, simple relations of the kind observed would be expected.

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* The sulphur molecule is assumed diatomic in the vapour state. *Cf.* C. Cuthbertson, Proc. Roy. Soc. A, lxxxiii. p. 151 (1909). B. Rosen, *Zeit. f. Physik*, xlviii. p. 545 (1928).

† Cf. *Zeit. f. Physik*, xxxi. p. 681 (1926).

These results may also be considered on the basis of the analogous expression given by the classical electron theory *, according to which

$$\frac{\mu^2-1}{\mu^2+2}=\frac{4\pi}{3}\cdot\frac{Ne^2}{m}\Sigma\frac{Z_p}{p^2-n^2}, \quad . \quad . \quad . \quad . \quad (2)$$

where Z_p is the number of quasi-elastically bound electrons of natural frequency p. If $p>>n$, the summation may be written $\Sigma\frac{Z_p}{p^2}$, and since p is smallest for the outer electrons, $(\mu^2-1)/(\mu^2+2)$ is proportional to Z_p.

In the case of HBr and Br_2 the same relation is not found between the refractivities which holds in the case of HCl and Cl_2, and a simple explanation is obtained from equations (1) and (2) above. In the case of bromine, there is absorption in the visible region of the spectrum, indicating that $p>>n$, so that a small change in p, which depends on the state of binding, may produce a large change in refractivity. Similarly for HI and I_2; iodine vapour has a large absorption in the visible region, and no simple relation is observed between the refractivities. In a note to 'Nature' † it was stated that the ratio of the refractivities of HBr and Br_2 is $(\frac{13}{25})$, which is equal to the ratio of the numbers of M and N electrons in the two molecules. Although the ratio $(\frac{13}{25})$ holds fairly accurately (see Table III.), since the M electrons in Br_2 and HBr are much more tightly bound ‡ than the N electrons, in view of the discussion above, it seems better to regard this agreement as a coincidence rather than as a statement of physical reality, and to consider that the "$(\frac{4}{7})$ relation" fails owing to absorption in the visible region.

In other molecules, where conditions are not so favourable as in HCl, Cl_2, and CCl_4, such simple relations are not found. In many cases, using arguments similar to those above, agreements can be obtained within 3 per cent. to 5 per cent., and in general the results are closer than those derived using an additive rule. It has not been thought worth

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* *Cf.* O. W. Richardson, 'Modern Electron Theory,' 2nd ed. p. 148.

† *Loc. cit.*

‡ *Cf.* values obtained for a constant ϵ proportional to the total energy of an electron for the different electrons in Rb^+ ion. There are the same number of electrons in Rb^+ as in Br^- (*vide* D. R. Hartree, Proc. Camb. Phil. Soc. xxiv. p. 111 (1928)).

while to discuss these results, for it is clear that the method is only approximate. In molecules such as the oxides of nitrogen and of sulphur and in organic compounds, it is evident on general grounds that the distribution and binding of the electrons are characteristic of the molecule as a whole and not of particular atoms in the molecule. In the case of CH_4, for example, it is obvious that the same kind of argument cannot be applied which is used for CCl_4. It is of interest to note that results * obtained from the X-ray examination of the crystalline compond $C_6(CH_3)_6$, in which the (CH_3) group is of crystallographic importance, are in agreement with the view that this group cannot be regarded mainly as a distribution of charge about the carbon nucleus, in which the hydrogen nuclei have little influence, but that there is a certain distribution of charge determined more or less equally by all the nuclei.

5. *Summary.*

In previous papers attention has been directed to the discrepancies between calculated and observed values of gaseous refractivities. In the present paper four simple relations are given between the refractivities of gaseous compounds, these relations holding fairly accurately.

A tentative explanation is given based on the numbers of loosely bound electrons, and it is shown that, if certain conditions are approximately satisfied, such simple relations might be expected both from the quantum theory and also from the classical theory of dispersion. It is realized that a simple explanation of this kind cannot be final; a more detailed explanation is required which will be applicable in the general case.

In conclusion I wish to take this opportunity to thank Mr. Herbert Bell and Mr. R. G. Wood for assistance in reading previous work on this subject, and Prof. W. L. Bragg, F.R.S., and Dr. E. C. Stoner for valuable criticism and suggestions.

University of Leeds,
Feb 12, 1929.

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* See a paper by Dr. Kathleen Lonsdale to be published soon by the Royal Society. I am indebted to Dr. Lonsdale for pointing out this interesting fact.

CIV. *Notices respecting New Books.*

Alternating Current Rectification. By L. B. W. Jolley. (Chapman and Hall, 11 Henrietta Street, Covent Garden, London, W.C. 2. Price 30*s*. net.)

THE revised edition of Mr. Jolley's work incorporates many of the important technical improvements in the design of rectifiers which have recently been made by British and foreign investigators. In addition to the types of rectifiers considered in the first edition, two or three supplementary chapters are devoted to wireless rectifiers and inverters. After consideration of valve and crystal rectification, it was natural that the question of high and low tension radio supplies should follow. The author deserves commendation rather than adverse criticism for the introduction of these important chapters. In the limited space at his disposal, the author has given the mathematical treatment required for the effective study of rectification. The bibliographies at the end of the chapters are of especial value for further study: references are given to original papers and to notices of these papers in Science Abstracts. Mr. Jolley's volume gives a comprehensive account of present-day practice and can be recommended as an up-to-date presentation of this branch of electrical engineering.

Statistical Mechanics with Applications to Physics and Chemistry. By R. C. Tolman. (The Chemical Catalog Company. New York, U.S.A. Price 5 $.)

This work, of special interest to students of chemistry, sets out the theory of statistical mechanics and discusses the many applications of this theory to both chemical and physical problems. The elements of the earlier quantum mechanics are introduced and applied to the particular cases of specific heats of gases and solids and the vapour pressure of crystals at very low temperatures. In addition to the chapters on molecular states and the absorption and emission of radiation, the author gives a very full treatment of the rates of physical and chemical processes, diffusion, evaporation, adsorption, solution, thermal and electrical conductivities. One chapter, based on the Arrhenius hypothesis of activation, is devoted to the temperature cœfficients of reaction velocities. Attention is called to the inadequacy of the hypothesis, *e.g.*, in the classical experiment of Gerlach and Stern on the magnetic orientation of silver atoms.

The rate and change of rate with temperature of photochemical reaction are next considered and brief references made to the effect of external electric and magnetic fields on molecular systems. Prof. Tolman's volume gives an excellent survey of the latest investigations in this branch of science, will enable the reader to study with profit more advanced treatises, and in indicating further directions of advance should promote research and assist in the development of this subject.

Materiewellen und Quantenmechanik, eine elementare Einführung. By Prof. ARTHUR HAAS. (Leipzig: Akademische Verlagsgesellschaft, M.B.H. Price 8 marks.)

IN 'Materiewellen und Quantenmechanik,' the author of the well-known 'Einführung in die theoretische Physik' has provided a concise and elementary introduction to the study of the theories associated with the names of de Broglie and Schrödinger. Eigen functions and Eigen values are illustrated by the simple cases of differential equations satisfied by Hermite's polynomials and Legendre's spherical harmonics, followed by application to the problems of Planck's oscillator and the hydrogen atom. The quantum mechanics of Heisenberg and the quantum statistics of Bose and Fermi are summarized, and brief references are given to the work of Dirac and others. The English translation of this excellent introduction to the modern theory of atomic dynamics will be appreciated by a wider circle of readers and deserves the favourable reception accorded to the authors' Introduction to Theoretical Physics.

The Chemical effects of Alpha Particles and Electrons. By S. C. LIND, Ph.D. [Second (revised and enlarged) edition.] (The Chemical Catalog Co. New York. Price 5 $.)

THE new edition of Dr. Lind's work has soon followed the publication of the first: in its revised and enlarged form the author has surveyed the theoretical and experimental results which have been published during the last few years. Among the subjects included in this second edition are the researches of Mund on the action of radon on gases and the equation for calculating ionization in large spheres, a formula of great importance and practical application; the work of Erikson and Wahlin on ion clusters; the author's experiments on the acceleration of acetylene polymerization by nitrogen ions, and the discovery that even inert gases like helium, argon, etc., contribute to the reaction in exact proportion to their ionization. Experimental tests of photochemical equivalence are described with brief references to the work of Taylor, Dickinson, Bonhoeffer, and others. Two useful indexes of authors and subjects are appended.

Catalysis in Theory and Practice. By ERIC K. RIDEAL and HUGH S. TAYLOR. (Macmillan & Co. Ltd., St. Martin's Street, London. Price 20*s.* net.)

THE first edition of this book appeared some nine years ago and received an appreciative notice in the pages of this Magazine. The volume of research in the theory and application of catalysis has expanded considerably since the publication of the first edition: the second edition, revised and enlarged, incorporates recent contributions to the study of catalysis, including the numerous researches of the two authors. This has necessitated the addition of new sections: as far as it is possible in this rapidly growing branch of chemical science, other chapters have been brought up to date. It is not without interest to note the association of the Philosophical Magazine with the progress made in the study of catalysis during the last hundred years. Nearly a century ago, papers were published by Faraday on his theory of passivity, by Henry on the combustion of carbonic oxide, and by Draper on photochemical reactions. Recently, contributions have been made by several research workers, including R. W. Wood, Rideal, Hinshelwood, and others.

Sound, a Physical Text-book. By E. G. RICHARDSON, B.A., M.Sc., Ph.D. (Edward Arnold and Co., 41 & 43 Maddox Street, London, W. 1. Price 15*s.* net.)

DR. RICHARDSON'S text-book is a welcome addition to the literature dealing with the subject of experimental acoustics. The results of recent experimental researches are reviewed and include the extensive work of Raman on the bowed string and of W. H. George on the struck string to discriminate between the Helmholtz and Kaufmann theories: some sections on various types of musical instruments are also included.

An elementary introduction to the theory of Prandtl on the motion of viscous fluids is followed by the discussion of eddies and vortices and Kármán's experimental verification for maximum stability. Under the heading of technology, the investigations of Sabine, Jäger, and others on the acoustics of buildings are noted, as well as the problems of sound ranging, direction finding, and other technical applications. Numerous references are given to original papers, especially those which have appeared during the last few years. A great amount of information is brought together in this book which will be of service both to degree students and research workers in this subject.

Alkaline Accumulators. By J. T. CRENNELL, B.A., and F. M. LEA, M.Sc., A.I.C. [Pp. x + 132, with 24 figures.] (London: Longmans, Green and Co. 1928. Price 10*s.* 6*d.* net.)

ON account of their mechanical robustness, suitability for varied and intermittent use, and freedom from injury by overcharging, alkaline accumulators possess distinct advantages over acid accumulators for such purposes as train lighting, electric traction, wireless batteries, or for any other purpose in which the regular charging and discharging which is necessary to maintain acid batteries in good condition is not possible. They are a comparatively recent development, and their advantages have not been as generally appreciated as they should be.

The volume under review should do much to counteract this state of affairs. The methods of construction of cells of the

Edison and Jungner types are explained, together with their advantages and disadvantages, and methods of operation and maintenance. The theory of the action which takes place on charge and discharge is carefully explained and attention is drawn to gaps in the theory. A fair balance between theory and practice has been preserved, and the volume is one which all who use alkaline accumulators should possess. It is to be hoped, moreover, that its publication will stimulate research in those directions in which the theory is still obscure.

Symbols and Formulæ in Chemistry. By R. M. CAVEN, D.Sc., F.I.C., and J. A. CRANSTON, D.Sc., A.I.C. [Pp. ix+220.] (London: Blackie and Son. 1928. Price 15*s*. net.)

IN this volume is given an account of the use of symbols in chemistry from the beginnings of the science down to the present day. Many of the early symbols are of no scientific value but are quaint or amusing and of antiquarian interest. The historical account of the beginnings of symbolism embodies the results of extensive research. The gradual development of modern symbols is traced and the application of theories of structure to structural formulæ is considered. Other subjects treated include an account of the development of stereochemistry, theories of valency, and the electron in chemistry. There is no reference to the important application of X-ray methods of analysis to the elucidation of the structure of crystals and of organic substances. The volume provides a general survey of great interest to the student of chemistry and of considerable value for purposes of reference.

The Theory of Determinants, Matrices, and Invariants. By H. W. TURNBULL, M.A. [Pp. xvi+838.] (London: Blackie and Son. 1928. Price 25*s*. net.)

THE first seven chapters of this book deal with the theory of determinants and of matrices, written mainly with a view to their applications in the remainder of the book. The theory of binary forms is then considered briefly, serving as an introduction to general and multilinear forms and the general properties of invariants. The applications of the theory to algebraic and differential geometry have been omitted, as well as the algebra of alternate numbers. An account is given of the more important recent work on the subject, including Weitzenböck's account of the basis of analytical projective geometry in relation to the usual metrical forms.

Both the direct and the symbolic methods are explained and used. The volume provides an excellent introduction to the subject, is well printed, and contains a number of illustrative examples. Recent developments in physics have attracted increased attention to the theory, and the publication of the volume comes at an opportune time.

1. *Untersuchungen zur Quantentheorie* von LOUIS DE BROGLIE. *Übersetzt* von Dr. W. BECKER. [Pp. iii+88, with 6 figures.] (Leipzig: Akademische Verlagsgesellschaft M.B.H. 1927. Preis M.5.80.)

2. *Four Lectures on Wave Mechanics.* By Dr. ERWIN SCHRÖDINGER. [Pp. viii+53.] (London; Blackie and Son, Ltd. 1928. Price 5*s.* net.)

3. *Collected Papers on Wave Mechanics.* By E. SCHRÖDINGER. Translated by J. F. SHEARER, M.A., B.Sc., and W. M. DEANS, B.A., B.Sc. [Pp. xiii+146.] (London: Blackie and Son, Ltd. 1928. Price 25*s.* net.)

4. *Selected Papers on Wave Mechanics.* By LOUIS DE BROGLIE and LÉON BRILLOUIN. Translated by W. M. DEANS, B.A., B.Sc. [Pp. viii+151.] (London: Blackie and Son, Ltd. 1928. Price 15*s.* net.)

WAVE MECHANICS as developed by Schrödinger, starting from ideas put forward by de Broglie, has attracted much attention in view of the success which it has achieved in explaining many quantum phenomena without introducing the idea of discontinuity. The theory is based on the analogy between the path of a ray of light and the path of a material particle: for dimensions comparable to the wave-length of light, the laws of geometrical optics no longer hold and undulatory optics must be used. Similarly, for dimensions comparable to the size of an atom, Newtonian dynamics no longer holds. Wave mechanics analogous to undulatory optics must be used.

(1) is a German translation of the original memoir of de Broglie, which appeared in *Annales de Physique*, 10, iii. This important paper is not included in (4), and those who read German with facility will welcome its republication in self-contained form.

(2) contains the substance of four lectures delivered at the Royal Institution in March, 1928. No better introduction to the theory can be recommended. This small volume is a masterly example of clear exposition, and in a few pages many of the successful applications of the theory are sketched.

(3) contains the translation of nine original papers by Schrödinger, which appeared during 1926 and 1927, arranged in chronological order. The study of this volume should follow the reading of (2). The papers have been reprinted without alteration, and it is of interest to follow the gradual development of the author's ideas. A somewhat detailed abstract of the contents, with references to the subsequent pages, enables the general line of thought to be clearly followed. The four principal papers on "Quantisation as a Problem of Proper Values" contain the main formulation of the theory. Another paper, entitled "On the Relation between the Quantum Mechanics of Heisenberg, Born, and Jordan, and that of Schrödinger" illustrates the close

relationship between wave mechanics and matrix mechanics, in spite of the widely differing initial assumptions.

(4) contains the translation of five original papers by de Broglie and of four by Brillouin which appeared, with one exception, during 1926 and 1927. Some of these papers summarize the investigations of de Broglie and Schrödinger and elaborate the connexion between wave and matrix mechanics. Of particular interest are the last two papers:—In "The Wave Mechanics and the Atomic Structure of Matter and of Radiation," de Broglie deals with the difficulty of reconciling the propagation of the waves of continuous amplitude of Schrödinger's wave mechanics with the atomic structure of matter and of radiation. He shows that continuous solutions provide only a certain statistical view of dynamical phenomena, the exact description of which probably requires the consideration of waves which admit of singularities. In "A Comparison of the Different Statistical Methods applied to Quantum Problems," Brillouin considers the differences between classical statistics and the methods of Bose and Einstein and of Fermi and Dirac; on certain assumptions the laws of emission and absorption of light stated by Einstein and their various generalizations are obtained.

CV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 760.]

February 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Basal Complex of Jamaica, with special reference to the Kingston District.' By Charles Alfred Matley, D.Sc., F.G.S. With Petrological Notes by Frank Higham, B.Sc., A.R.S.M., F.G.S.

The author deals with the problem of the age of the old rocks of Jamaica, in the light of the results of detailed stratigraphical work in the Kingston district. The geological surveyors in 1859–66 recognized no rocks older than Cretaceous, and regarded the Jamaica 'granite' as Tertiary; and the same views were strongly expressed by R. T. Hill in 1899.

In the Kingston district and the country east of it the author finds a Basal Complex of great thickness, unconformably underlying Upper Cretaceous and Eocene rocks. The 'granite and syenite' of the Survey—chiefly a granodiorite—does not penetrate the Tertiary 'White Limestone', as has been asserted, but is an important plutonic member of the Basal Complex, and contributes abundant pebbles to overlying Upper Cretaceous and Eocene conglomerates. Another plutonic member of the Complex is a peridotite of Harzburg type, now converted to serpentine.

The other members of the Complex, many of which are found in a metamorphic condition, were originally sediments and volcanic lavas and tuffs. They include marbles, schists of varied composition, amphibolites, granulites, and hornfelses. The schistose structure is chiefly the result of dynamic metamorphism acting on a series of limestones, calcareous mudstones, shales, sandstones, basic lavas, and tuffs. The less altered lavas and intrusives range from acid to basic. There is evidence that the contact-altered granulites and hornfelses had suffered from earth-movement before the granodiorite invaded them. As the metamorphism antedates Upper Cretaceous time, it is suggested that it is late-Palæozoic (Hercynian) or even older. No trace of fossils has been found in the Complex.

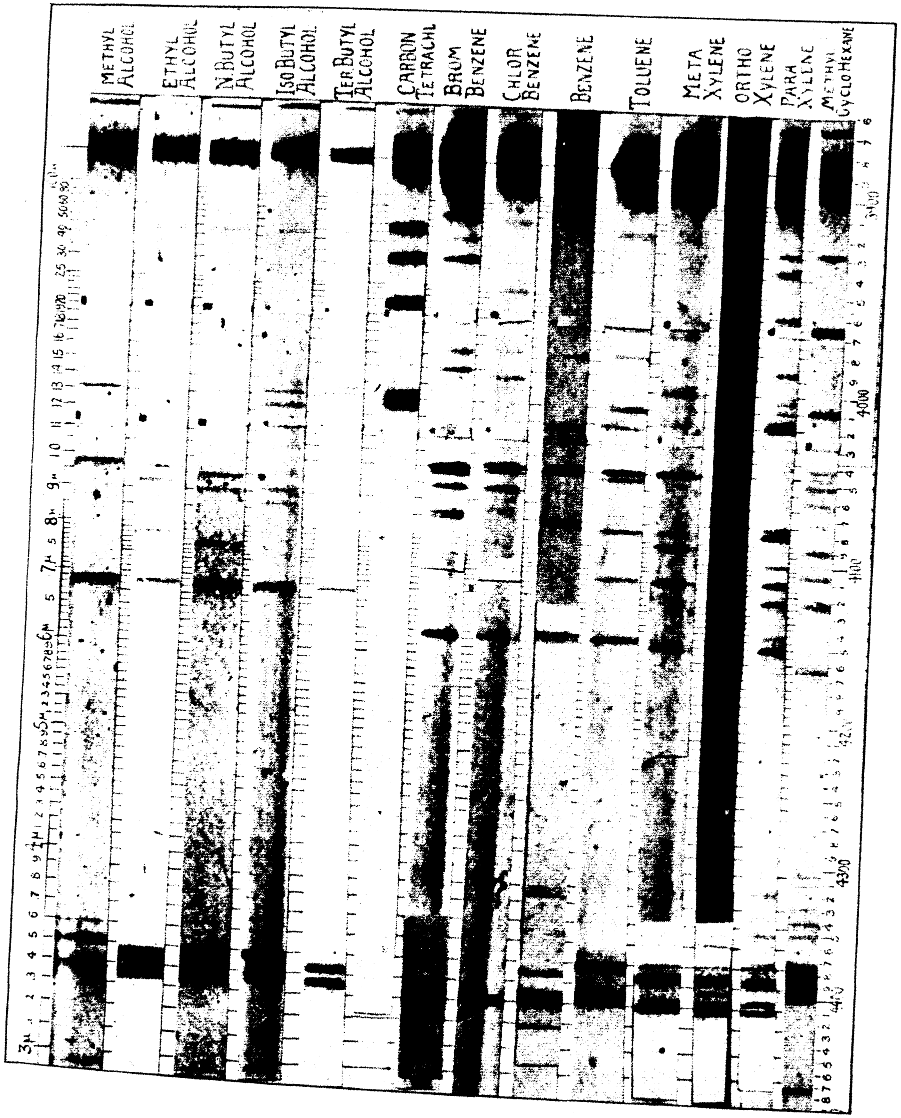
The rocks of the Complex have been involved with Upper Cretaceous and Eocene strata in the later (Tertiary) movements that formed the Blue Mountains, and their separation from the latter needs detailed field examination, owing to the complicated stratigraphy. For example, a lenticular strip, 3½ miles long, in the Upper Yallahs valley, has been brought up on a thrust-plane and driven east-north-eastwards over a sigmoidal fold of Eocene rocks. Mylonization is traced along this thrust and elsewhere.

A group of red-weathering andesitic lavas and tuffs, with associated intrusives, are described. They underlie the Upper Cretaceous conglomerates, but it is not yet known whether they are of Cretaceous age or belong to the Complex.

Comparison is made with similar rocks in Cuba, Hispaniola (Haiti and Santo Domingo), Porto Rico, and the Virgin Islands. The asserted absence of pre-Cretaceous rocks in Porto Rico is discussed. With the exception of Porto Rico, Jamaica now falls into line, as regards the presence of a pre-Cretaceous basement, with the other islands of the Greater Antilles, although there is still want of agreement as to the ages of the rocks of that basement.

In the Appendix Mr. Higham deals with the petrology of the Complex, and compares the major intrusives with those in the other islands of the Greater Antillean group, in which the igneous history is very similar. The serpentines are regarded as earlier intrusions, the later activity being accompanied by intrusions of the calc-alkaline suite characteristic of the Andes. Evidence of consanguinity is also afforded by the constancy of titanium-minerals and the presence of clear colourless augite, which is often the primary mineral in the granodiorites.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]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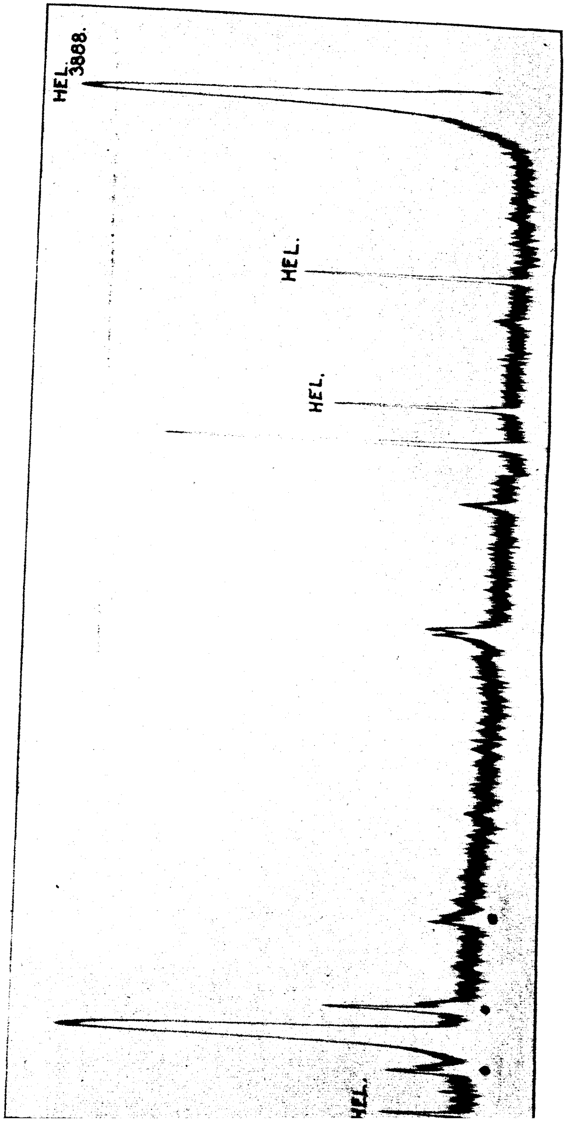
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THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

SUPPLEMENT, JUNE 1929.

CVI. *A Molecular Theory of Friction. By* G. A. TOMLINSON, *B.Sc.* (*of the National Physical Laboratory*) *.

1. IT is now generally agreed that friction is, in some way, a consequence of the forces which molecules exert on one another when sufficiently close together. It is known that two molecules can exert a strong attraction on each other, and there is evidence of various kinds that the field of attraction probably extends to a distance of several times the molecular diameter, the force being a rapidly diminishing inverse function of the distance between the molecules.

Since the molecules of a solid are in a state of equilibrium, we have also to recognize the existence of a repulsive force between them, counteracting the cohesive attraction. There is little or no experimental information concerning this repulsive force, but there is certain indirect evidence that the force increases from zero very abruptly when two atoms approach to a critical distance. The highly stable equilibrium which exists amongst the atoms of a metal can only be explained by supposing that the rate of change of the repulsion is much greater than that of the attraction, when the atoms are drawn apart slightly by an elastic strain. The work of Born and Landé † and others on the energy of the crystal lattice led to similar conclusions. A similar conception has been advanced in recent years by various other physicists, including Lennard Jones* and T. W. Richards†.

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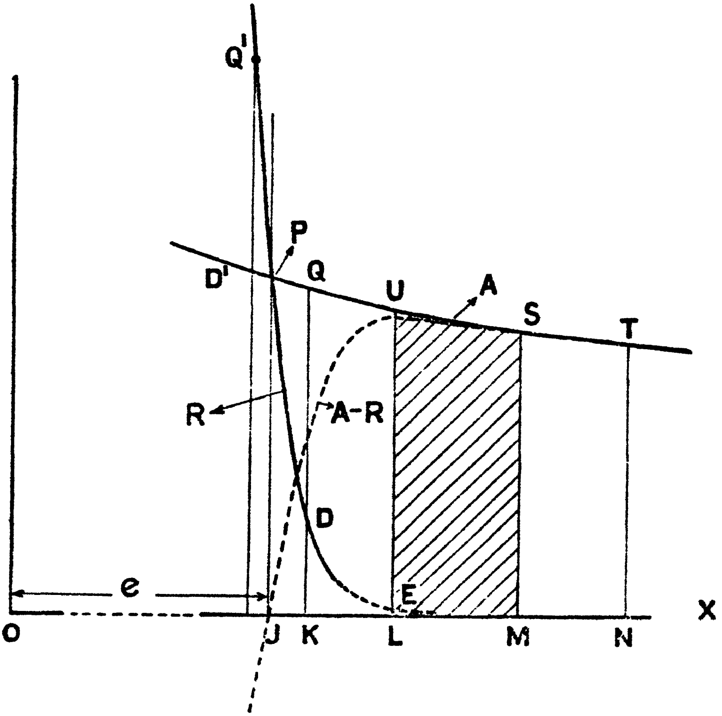
* Communicated by Sir J. Petavel, K.B.E., F.R.S.

† *Deut. Phys. Gesell.* (1918).

The present paper contains a tentative theory of dry solid friction based upon the assumed existence of molecular attractions and repulsions having such characteristics, as shown diagrammatically in fig. 1 by the curves A and R. These curves represent descriptively the supposed attraction and repulsion as functions of the distance between the molecules. No assumptions need be made as to the form of the curves, but the slope of the repulsion curve is assumed to be much greater than that of the attraction curve, and the effective range is supposed to be much less; in fact, considerably smaller than the dimensions of the molecules.

Fig. 1.



Because of the very limited present knowledge concerning interatomic forces, such a theory must necessarily be to a large degree speculative, and its proper place in this paper should be at the end, as a suggested explanation of the experimental work. But although the experiments to be described in the paper may be regarded as having some general interest, they would exhibit no particular connexion with each other, apart from their relation to the tentative theory, the probability of which they were designed to test. It therefore seemed preferable, in order to admit of an adequate seriatim discussion of the results, to give first a preliminary description of the theory, the details of which are further discussed in relation to the several experiments to be described.

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* Proc. Roy. Soc. cxii.

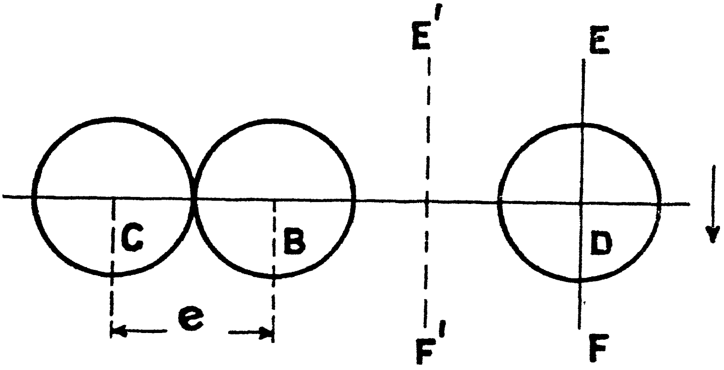
† Journ. Amer. Chem. Soc. xlv. to xlviii.

Consider two solid bodies in contact and with relative sliding motion. By our hypothesis, only a certain number of molecules of the one body will approach those of the other body sufficiently closely to suffer repulsion, as any material surface will have quite a coarse structure compared with the range of the repulsive force. Many other molecules of one body may experience some attraction towards the molecules of the other body without entering the repulsion field at all. The applied force between the bodies, together with the sum of all the cohesive attractive forces, is supported by the sum of all molecular repulsions. (Some very anomalous cases of friction are described later in the paper in which the cohesive attraction between the two bodies produces an important effect on the friction. Normally such attractions are negligible by comparison with the applied force.) As the two bodies move relatively, there is a continuous change taking place in the pairs of molecules bearing the load, and the theory assumes that when two molecules come into contact, *i.e.*, come into each other's repulsion field, and then separate, a loss of energy occurs which is manifest as friction. The theory makes no assumptions regarding the cause of the attractive and repulsive forces, but treats the molecules as if they were simple centres of fields of force. Also the ultimate distribution of the lost energy amongst the various possible degrees of freedom is not considered in the theory, which deals solely with the molecular mechanism by which work may become transformed into heat.

It is difficult to understand how friction could be explained as a loss of energy occurring when two atoms approach within each other's attraction field alone. Consider for simplicity a single atom D (fig. 2) forming part of a body which is moving in the direction of E F past another body, of which B and C form two atoms in the state of equilibrium characteristic of a solid. Referring to the curves A and R of fig. 1, the point P corresponds to the initial undisturbed condition of the atom B, which takes up a position at a distance of O J from C such that the attraction and repulsion on it are equal and opposite and of amount P J. We may observe the very stable condition which follows from the assumed rates of change of the two forces. A small displacement of B in either direction from the point J is accompanied by a strong restoring force.

Let us suppose that the atom D in moving past B along the line E F approaches B to within a distance such as O N in fig. 1; that is, within the attraction field but outside the range of the repulsion. The passage of A will cause a slight disturbance in the position of B, which will move away from C, supposing C to be fixed, to a distance O K in fig. 1 such that the net force Q D now exerted on B by C equals the attraction T N of atom D. The atom D in proceeding further along E F then withdraws from B, which returns to its initial position. It is conceivable that B arrives back to its original position with some appreciable velocity and therefore with some added energy, the aggregate of which might correspond to the loss of energy in friction. If this were the case, however, the energy imparted to B would be reduced as the velocity of relative motion of the two bodies was reduced. But in moving two actual bodies over one another the same total number of atomic approaches would occur whatever the velocity of motion, and therefore the work done, and consequently the coefficient of friction, would be reduced continuously as the velocity was reduced. This is quite contrary to experience. On the other hand, it

Fig. 2.



known that the characteristic atomic frequency of most of the elements is of the order of 10^{13} per second; and it seems probable that on account of its extremely small natural period, the displacement of the atom B will follow the increase and decrease of the attraction of D in an almost perfectly dead-beat manner. In other words, the mechanical work done on the atom D by the attraction during its approach does not differ materially from the work done by D against the attraction during its recess.

To explain friction it appears necessary to suppose the existence of some irreversible stage in the passage of one atom past another, in which heat energy is developed at the expense of external work. It is possible to suggest a means by which this may happen in the case of those atoms which come near enough together to experience repulsion.

Let us now consider the atom D as passing by the elementary body B C along a nearer line E′ F′ and approaching so close that D and B come into mutual repulsion. As D approaches, the two atoms will exert an increasing attraction, and under this force B will move away slightly from C as before. This process continues until the atoms are separated by a distance O L in fig. 1, at which distance $\frac{dA}{dx}=\frac{dR}{dx}$, A and R denoting the forces of attraction and repulsion. At this period A−R has a maximum value and B is equidistant from D and C. As D approaches still nearer, the symmetrical position of B will be maintained, since for all positions to the left of L, $\frac{dR}{dx}$ exceeds $\frac{dA}{dx}$, and the symmetrical position is one of stable equilibrium. A small movement of D then brings both pairs of molecules into the position corresponding to the point P, *i. e.*, B occupies its original position relative to C with D added to it in a similar stable relationship. Any approach of D now brings into play a powerful net repulsion such as is shown by Q′D′, and this is supposed to be the condition of those molecules which are assisting to support the external load applied to the contact surfaces.

Consider next what occurs when the molecule D is withdrawn. Up to the position corresponding to the point L, the molecule B remains in stable equilibrium equidistant from D and C, and everything up to this point is reversible. At the point L the equilibrium of B changes from a stable into an unstable condition. As this transition is smooth and continuous, there will be a certain probability that the molecule B will persist in its symmetrical position of equilibrium as D recedes, until B is at some distance O M from both C and D, when, owing to its instability, B will suddenly fly back to its position of stable equilibrium at a point between J and L. This point, in fact, is the same that B occupied when D in its approach was at the same point that it is now supposed to occupy in recess.

The molecule B thus returns to its stable position with a store of kinetic energy equal to the area U S M E, this being the work done on B by D during the irreversible portion of the cycle from L to M. We thus have a possible mechanism by which the recession of two molecules is not the reverse of their approach, but contains an irreversible stage in which mechanical work is transformed into molecular kinetic energy or heat.

According to the theory suggested, friction is in a sense a matter of chance, as the displacement L M of the molecules into the unstable region may vary greatly. Actually we are concerned with the statistical average of a very great number of different values, and the uniformity always observed in experiments on friction is due to the large number of molecules in contact. It may be remarked that on this theory the two bodies in contact become virtually united at all the points where atomic repulsion occurs, by the formation of a continuous chain of atoms in stable equilibrium. On severing the atomic bond the plucking action of one atom on the other dissipates a quantity of energy which is independent of the velocity of relative motion, and in this respect the theory is in agreement with experiment. Further, only those atoms which contribute to the elastic reaction, and so help for a short time to support the load, pass through the irreversible stage and so involve friction. This is again in conformity with the fact that the friction is proportional to the load.

In the simple case we have considered in fig. 2 it will be seen to be a matter of chance whether the atom B ultimately attaches itself to C or to D. In the case of actual bodies there seems to be little doubt that the disturbed atom has a strong bias in favour of a return to its original position, and probably nearly all do so. Some, however, definitely do not—a question which is discussed later.

2. We shall next obtain an expression for the coefficient of friction. The force F between the surfaces is supposed to be supported by the sum of the molecular repulsions

$$F=\Sigma\,(p).$$

Since the force of repulsion varies very rapidly with distance, the individual values of p must vary widely from one place to another and from one instant to another, but a very large number of molecules are concerned under conditions which justify us in assuming the total number n to be statistically constant so long as the load is constant. This being so, we can assign a statistical average value $\bar{p}$ to the force of repulsion of a pair of molecules, and we then have

$$F = n\bar{p}.$$

The actual value of n will depend on the total load and the shape of the contact surfaces.

As one body slides over the other, a continuous exchange of partners will proceed amongst the repelling molecules. Some will pass out of the repulsion range and others will enter it. At each approach and separation a loss of energy occurs, of which the average value will be called W.

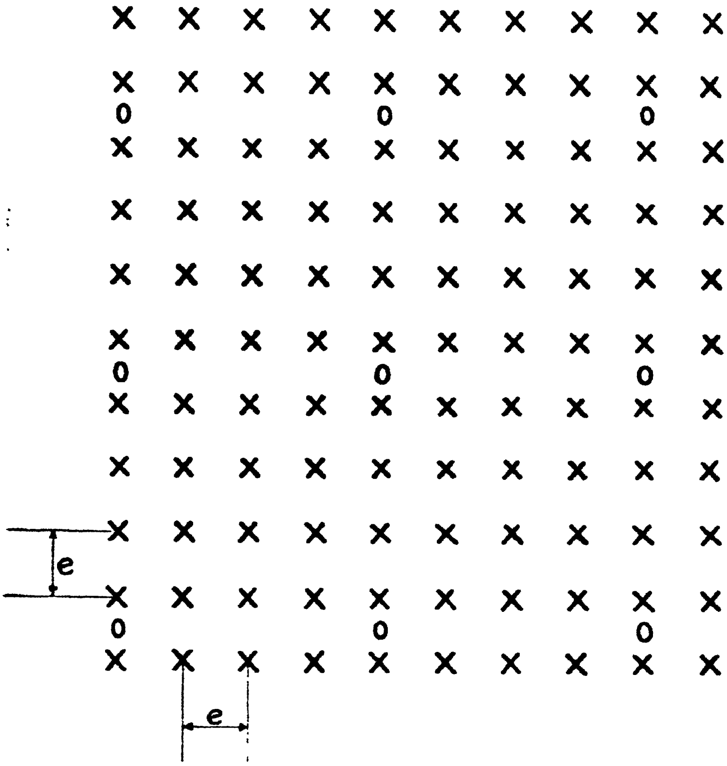
If we can find an expression for the total number N of separations taking place in a movement x, we can equate the loss of energy to the external work done :

$$NW = \mu Fx.$$

If, for the moment, we imagine the molecules to have a perfectly definite array, we can represent the circumstances, for example, by fig. 3, where the crosses represent the whole of the molecules of one surface, and the circles the proportion of molecules on the second surface which contribute to the repulsion. If the two patterns are moved relatively to each other, say vertically up the page, through a distance x, which is large compared with e, it is evident that the number of separations which will occur is $n \times \frac{x}{e}$ n being the total number of circles. It may be noticed that in the theoretically ideal distribution shown in the figure we should get a different number of separations if the relative motion of the two bodies were in a different direction—*e. g.*, if the motion were at 45°, the number would be $n \times \frac{x}{\sqrt{2}e}$. There is some evidence, as a matter of fact, that friction between crystalline surfaces may depend on the direction of relative motion.

In any ordinary case, however, the general distribution of the molecules in the surfaces and of the individual molecules concerned in the repulsion at any moment will be quite irregular, and we assume, moreover, that the surfaces will have a coarse structure in comparison with the extent of the repulsive field. There must, however, be a sufficient number of molecules within the repulsive range at any moment to support the load, and the conditions will be statistically constant, so that we may reasonably assume that the number of separations in distance x will be

Fig. 3.



$$N = q \times n \times \frac{x}{e},$$

where e is the *mean* molecular distance and q a statistics constant whose actual value must remain unknown, but probably not very widely different from unity.

We then have

$$NW = \mu Fx = \mu npx,$$

also $$\mathrm{NW}=q\frac{nx}{e}\mathrm{W},$$

and hence $$\mu=\frac{q\mathrm{W}}{\bar{p}e}. \quad (1)$$

Remembering our initial assumptions as to the nature of the molecular attraction and repulsion, we can express W approximately in terms of the normal cohesive attraction and the average displacement $\bar{l}$ of the molecule into the unstable region of equilibrium (LM of fig. 1). Thus, if we take the force of attraction acting over the small displacement $\bar{l}$ to be a constant force A_0 slightly smaller than the normal cohesion P J of fig. 1, and neglect the small repulsive force acting between L and M, we get as a somewhat free approximation

$$\mathrm{W}=\mathrm{A}_0\bar{l}$$

and $$\mu=q\frac{\mathrm{A}_0\bar{l}}{\bar{p}e}, \quad (2)$$

a form of expression of more interest than (1).

The result obtained from the theory is so far in agreement with the experimental laws of friction; viz., that the friction is proportional to the load, independent of the area in contact and independent of the velocity of motion.

Further, in the expression for μ, A_0 and $\bar{p}$ may be regarded as molecular elastic constants which must have some association with the ordinary elastic constants of the material. The theory therefore suggests that the coefficient of friction should be related to the elastic constants. This has been investigated experimentally and a definite relation discovered. A discussion of this follows in section 8.

3. The foregoing theory will now be applied to the case of rolling friction. Consider a cylinder of radius r and length b rolling through a distance x on a horizontal plane surface under a load F. Let P be the force to be applied at the axis of the cylinder parallel to the plane to overcome the friction. Then the coefficient of rolling friction will be defined as

$$\lambda=\frac{\mathrm{P}}{\mathrm{F}}.$$

Making the same assumptions as before, we require to find the total number of molecular separations which occur in rolling a distance x. It is known that the cylinder and plane come into contact over a parallel strip of width $2a$ which can be determined. The intensity of normal stress is a maximum at the centre of the strip, and falls off to zero at the edges according to the equation

$$\left.\begin{aligned} f &= \frac{3}{2} f_{\text{mean}} \sqrt{1-\frac{y^2}{a^2}} \\ &= \frac{3}{2}\frac{F}{2ab} \sqrt{1-\frac{y^2}{a^2}} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (3)$$

where y is the distance from the centre of the strip.

The maximum stress intensity at the centre strip is thus

$$f_{\text{max.}} = \frac{3}{4}\frac{F}{ab}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In rolling a distance x a rectangular area bx is swept out, and every portion of this area comes in turn under the normal stress $f_{\text{max.}}$ Small end-effects are rendered negligible if b and x are supposed to be large in comparison with a. Hence the aggregate force which is applied and removed is

$$\frac{3}{4}\frac{F}{ab}\,bx = \frac{3}{4}\frac{Fx}{a}.$$

If we had again the ideal geometrical arrangement of molecules in rows, the number of separations associated with the application and removal of this load would be given by the equation

$$n\bar{p} = \frac{3}{4}\frac{Fx}{a}.$$

But as the surfaces in contact are continuously changing by the rolling motion just as in the preceding section they were changed by sliding, and the same irregular distribution of the repulsions exists, the actual number of separations will be qn, q being the same statistical factor as before, since both sliding and rolling have the similar effect of bringing a sequence of different but statistically equivalent molecular distributions into contact.

Hence the loss of energy

$$\begin{aligned} &= qn\mathrm{W} \\ &= \frac{3}{4}\frac{Fx}{a\bar{p}}\,q\mathrm{W} \\ &= \frac{3}{4}\frac{Fxq}{a\bar{p}}\,A_0\bar{l}. \end{aligned}$$

Equating this to the external work done,

$$Px = \lambda Fx = \frac{3}{4}\frac{Fxq}{a\bar{p}} A_0\bar{l}.$$

Or
$$\lambda = \frac{3}{4}\frac{qA_0\bar{l}}{a\bar{p}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This expression for the coefficient of rolling friction is very similar in form to equation (2) for the coefficient of sliding friction. In fact, by the present theory rolling and sliding friction are regarded as being identical in nature, a question which is discussed at more length in section 9.

4. The theory of friction outlined above is admittedly somewhat abstract and speculative. It is a remarkable fact, however, that a phenomenon so universal and important as the friction between solid bodies has so far received no satisfactory explanation. This, together with the fact that the present theory is supported in a number of ways by the results of experiment, appears to justify its presentation as a tentative explanation of friction. The experimental work will now be reviewed.

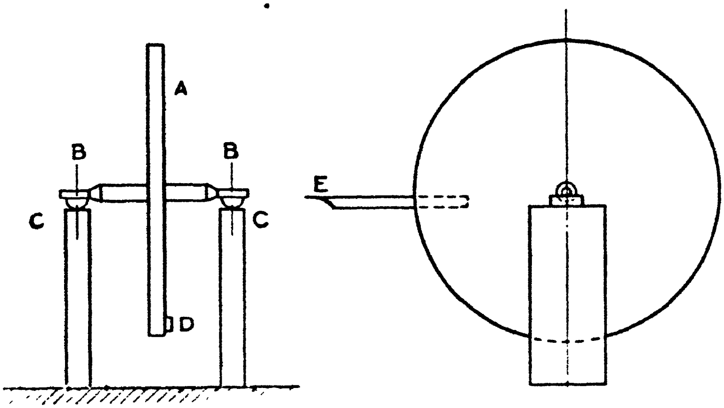
In the first place it may be noticed that the two expressions which have been derived from μ and λ each contain certain quite unknown quantities q, A_0, $\bar{p}$, and l. If, however, we take the ratio of λ and μ we get

$$\frac{\lambda}{\mu} = \frac{3}{4}\frac{e}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which all the unknown terms disappear, and a definite relation between λ and μ is obtained. In order to test this relation by experiment, the coefficient of rolling friction in a particular case was carefully determined. For this purpose a ground-steel disk A (fig. 4) was mounted on a spindle having hardened ends B ground and lapped to a diameter of 0·1 in. These lapped ends rested on two hard steel pads C in the form of semi-cylinders with the plane lapped face uppermost. The axes of the two pads were placed at right angles to the axis of the spindle, this geometrical arrangement ensuring that the bearing of the spindle on the flat face is uniform. This disk was given a small oscillatory motion rolling on the two pads. A small mass D was attached to the disk so that it could make slow vibrations as a pendulum. A light pointer E was attached to the disk, and an image of this was projected on to a screen magnified 50 times. With the disk oscillating slowly the successive semi-amplitudes were marked off at the rest positions of the image of the pointer on the screen. In this way the decrement of the amplitude was accurately measured, and from this friction could be found. The resistance of the air was examined by conducting a similar experiment having the disk suspended with its axis vertical on a torsional suspension of piano wire, giving the same frequency of oscillation. It was found that the contribution of the air resistance to the total friction measured in the rolling experiments was negligible. The rolling surfaces were thoroughly cleaned with alcohol-ether-ammonia cleaning mixture before the measurement.

The results obtained are given in Table I.

Fig. 4.



The theoretical relation in equation (6) may be used to calculate λ in terms of μ, for comparison with the above experimental result. As regards the value of e, the distance between the atoms, X-ray measurements give the lattice constant of iron to be $2{\cdot}86 \times 10^{-8}$ cm., and this value will be used for e.

The value of $2a$ can be found from equation (7) following, and is given in Table I.

Hence
$$\frac{\lambda}{\mu} = \frac{3 \times 2{\cdot}86 \times 10^{-8}}{4 \times 4{\cdot}14 \times 10^{-4}} = 0{\cdot}519 - 10^{-4}.$$

For clean dry steel Sir William Hardy has found $\mu = 0{\cdot}79$, and the writer has obtained a value 0·39 (see Table VI.): substituting these values, λ is found to be 0·000041 or 0·000020 respectively. If these are compared with the first three observed values of λ in Table I., a satisfactory order of agreement is found, especially in the case of the higher value of μ. It is considered preferable to exclude the last two observed values from this comparison, for reasons discussed later in section 6.

TABLE I.

Diameter of cylinders 0·1000 in.
Length of cylinders in rolling contact 0·100 in.
Total weight 600 gm.
Width of contact area, $2a=8{\cdot}28\times10^{-4}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cm.	radians.	
0·0090	0·0707	0·000047
0·00506	0·0398	0·000041
0·00135	0·0106	0·000045
0·00038	0·0030	0·000015
0·00024	0·0019	0·000011

5. Some further experimental results on rolling friction will now be examined, and will be shown to be in close agreement with the theoretical expression deduced for the coefficient. The quantity a which occurs in this expression can be found from the equation given by Hertz in his theory of elastic contact :

$$a^2=\frac{1}{\pi}\mathrm{F}r(\vartheta_a+\vartheta_b) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

r = radius of cylinder,
F = load on the cylinder per unit length,
$\vartheta=\dfrac{3\mathrm{K}+4\mathrm{C}}{\mathrm{C}(3\mathrm{K}+\mathrm{C})}$,
C = modulus of rigidity,
K = modulus of compressibility.

The suffixes a and b refer to the two materials forming the roller and the plane.

Where these are both the same we have

$$a^2=\frac{2}{\pi}\mathrm{F}r\vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Hence, using equation (6), which is cleared of all the unknown terms, for the value of λ in terms of μ, we have

$$\lambda=\frac{3}{4}\frac{e\mu}{a}=\frac{3}{4}\sqrt{\frac{\pi}{2}}\frac{e\mu}{\sqrt{\mathrm{F}r\vartheta}}. \quad . \quad . \quad . \quad . \quad (9)$$

This equation indicates that λ is not a constant, but is inversely proportional to $\sqrt{\mathrm{F}}$ and to $\sqrt{r}$.

Goodman * carried out an extensive investigation on rolling friction, employing commercial ball and roller bearings, and he arrived at the following conclusions :—

TABLE II.

Load F in lb.	Coefficient of rolling friction.	Coefficient of friction × $\sqrt{\mathrm{F}}$.
1000.........	0·0040	0·1265
2000.........	0·0028	0·1252
3000.........	0·0023	0·1260
4000.........	0·0020	0·1264
5000.........	0·0018	0·1273
6000.........	0·0016	0·1239
7000.........	0·0015	0·1254
8000.........	0·0017	0·1520
9000.........	0·0017	0·1613
10,000.........	0·0018	0·1800

(1) The coefficient of friction decreases as the load increases.

(2) The coefficient of friction decreases as the radius increases.

(3) The coefficient of friction is nearly independent of the speed.

These conclusions agree qualitatively with equation (9), but the theory can be tested further as regards the variation of the coefficient of friction with load by comparison with Goodman's results. In Table II. the first two columns are

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* Proc. Inst. Civil Eng. 1911-12.

taken from Goodman's paper, and the third column has been computed by the writer. The measurements were made on a roller bearing having rollers $\frac{3}{4}$ in. in diameter and 6 in. in length. The speed of the shaft was 80 revolutions per minute and the bearing was run without lubricant.

The last column shows that over a wide range of loads the theoretical relation between the load and the coefficient of friction is in very good agreement with the experimental results.

6. If the foregoing theory of friction is substantially correct an interesting deduction may be made. If two surfaces have a relative oscillatory motion, either sliding or rolling, and it is possible to reduce the amplitude to such an extent that the displacement of the surfaces or some portion of them becomes comparable with $\bar{l}$, we should find that an increasing proportion of the molecules would return through the unstable stage to the stable condition of equilibrium without being released with increased kinetic energy. Or we should expect the friction to become progressively smaller as the amplitude diminishes below a certain value. Such a result has, in fact, been obtained for both sliding and rolling friction in some experiments which will now be described.

A very light oscillator, made from a piece of cork, was pivoted on the point of a fine needle on a polished steel flat surface. A small piece of mirror was attached to the cork and also a piece of magnetized sewing-needle to provide a suitable control couple. The oscillator was contained in an exhausted vessel having a plate-glass window. The oscillations were observed by a reflected image of a cross-line on a remote scale. An oscillation was started by disturbing the magnetic field slightly, and the successive amplitudes were measured at the scale.

It can be shown that the amplitude will decrease uniformly if friction is constant. Thus let θ_1 and θ_2 be two successive amplitudes. Then the energy lost in friction is

$$c(\theta_1+\theta_2),$$

where c is a constant.

This is equal to the change in potential energy of the system, or

$$c(\theta_1+\theta_2)=\tfrac{1}{2}k(\theta_1^2-\theta_2^2),$$

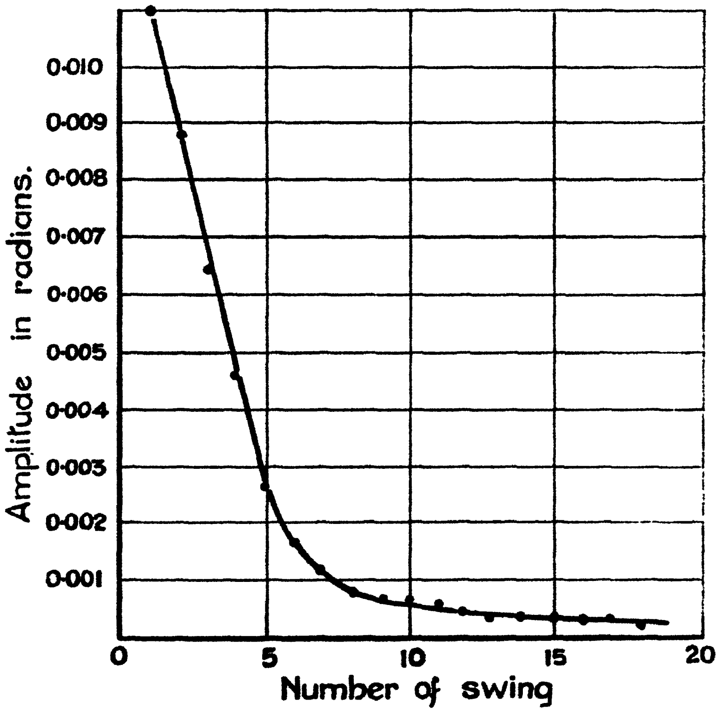
where k is the stiffness of the controlling couple.

Hence $$\theta_1-\theta_2=\frac{2c}{k}=\text{constant}.$$

The actual result obtained is very different, as shown by the curve in fig. 5, in which there is a well-defined deviation from the straight line at a certain amplitude, followed by a rapidly diminishing friction couple.

It is interesting to make an estimate of the relative linear displacement of the surfaces corresponding to the knee of the curve.

Fig. 5.



In an investigation into the deformation of instrument pivots at the National Physical Laboratory, Stott has found that a small flat is produced, the area of which over a wide range of loads is proportional to the load, or a definite flow-stress exists which is constant for any load. The value of this stress is found by Stott to depend somewhat on the angle of the pivot, and for the present purpose an assumed stress of 500 kilogrammes per square millimetre will be a fairly probable value. The weight of the oscillator was 0·15 gm., and the radius of the small flat, if it is assumed to be circular, is therefore about 3×10^{-5} cm

The bend in the curve corresponds approximately to an amplitude of about 0·0015 radian, so that the motion at the edge of the contact flat is about $4{\cdot}5\times10^{-8}$ cm. This is an amount of nearly the same magnitude as the distance between the atoms as found by X-ray measurements. The linear motion decreases uniformly to zero from the periphery to the centre, and the reduction in friction probably commences at the centre of the compressed area, spreading outwards more and more as the amplitude decays away. Hence the critical amplitude at which the friction begins to diminish is apparently an amount well below atomic dimensions.

TABLE III.

Rolling friction of two crossed cylinders 0·1 in. and 0·4 in. diameter.
Total weight 600 gm.
Major semi-axis of contact of ellipse, $5{\cdot}95\times10^{-3}$ cm.
Minor semi-axis of contact of ellipse, $2{\cdot}4\times10^{-3}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cm.	radians.	
0·00845	0·0665	0·000014
0·00720	0·0567	0·000013
0·00561	0·0442	0·000012
0·00276	0·0217	0·000010
0·000635	0·0050	0·000006
0·000237	0·00187	0·000004

In the case of rolling friction a similar result has already been obtained, as shown in Table I., where the coefficient of rolling friction decreases to about a quarter of its initial value when the amplitude becomes very small. This decrease was always observed in measurements of λ, and two further examples are given in Tables III. and IV. In the first case the 0·1 in. diameter cylinders are rolling upon two other cylinders of 0·4 in. diameter set at right angles to the axis of rolling.

In the second case two 3½-mm. steel balls are rolling on flat steel surfaces.

7. The measured coefficients of friction for three different types of rolling, given in Tables I., III., and IV., can be compared with the relative values of the coefficients found from the theoretical expression for λ, as a further test of the probable validity of the theory.

It will first be shown that equation (5) applies equally in all these cases of rolling.

In general, the contact area is an ellipse having semi-axes, *b*, parallel to the axis of rolling, and *a*, parallel to the path of rolling. Let *a* and *b* correspond to X and Y axes respectively, then the normal contact-stress is given by

TABLE IV.

Rolling friction of 3½-mm. steel ball on steel plane.
Total weight 600 gm.
Radius of contact circle, $3{\cdot}3 \times 10^{-3}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cms.	radians.	
0·0077	0·0605	0·0000165
0·0067	0·0528	0·0000155
0·00404	0·0318	0·0000125
0·00086	0·00675	0·0000048
0·000442	0·00348	0·0000030
0·000232	0·00183	0·0000017

$$f = \frac{3}{2}\frac{\mathrm{F}}{\pi ab}\sqrt{1-\frac{x^2}{a^2}-\frac{y^2}{b^2}}, \quad . \quad . \quad . \quad . \quad (10)$$

and the mean stress along the Y axis, parallel to the axis of rotation, is

$$\frac{\int_0^b f\,dy}{\int_0^b dy} = \frac{\frac{3}{2}\frac{\mathrm{F}}{\pi ab}\int_0^b \sqrt{1-\frac{y^2}{b^2}}\,dy}{b}$$

$$= \frac{3}{8}\frac{\mathrm{F}}{ab}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence, as in section 3, the total load applied and removed in rolling through a distance x is

$$2bx \times \frac{3\,\mathrm{F}}{8\,ab} = \frac{3}{4}\frac{\mathrm{F}x}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

which is the same result as that previously obtained for the rolling of a cylinder on a plane, that being only a particular case.

According to the theory, therefore, the relative coefficients of friction should be inversely proportional to the values of a. These have been calculated, and the results are summarized below.

TABLE V.

Type of rolling.	a. cm.	Theoretical, λ.	Measured, λ.
A. Cylinder on plane	$4{\cdot}14 \times 10^{-4}$	0·000041	0·000047
B. Cylinders on cylinders...	24×10^{-4}	0·000007	0·000013
C. Spheres on plane	33×10^{-4}	0·000005	0·000016

The theory thus shows that the rolling friction in cases B and C should be about $\frac{1}{6}$ and $\frac{1}{8}$ respectively of that of case A. Although the measured values are considerably smaller, there is some discrepancy in the relative values as compared with the theoretical values. These is reason for this, however, in the fact that cases B and C are not exactly examples of pure rolling.

Heathcote * has pointed out in connexion with the friction of ball bearings that some relative sliding motion must take place continuously at the contact. In fig. 6 a sphere rolling on a plane is shown. Different parts of the sphere between a and b are at slightly different radii from the axis of rotation, and therefore must have different peripheral velocities, leading to a distribution of relative sliding somewhat as shown in the diagram. There are two symmetrically-placed belts along which no slipping occurs, and inside the belts the surface of the ball slips backwards, while outside the belts the slip is forwards. The form of these belts shown is purely conjectural, but their existence has been demonstrated

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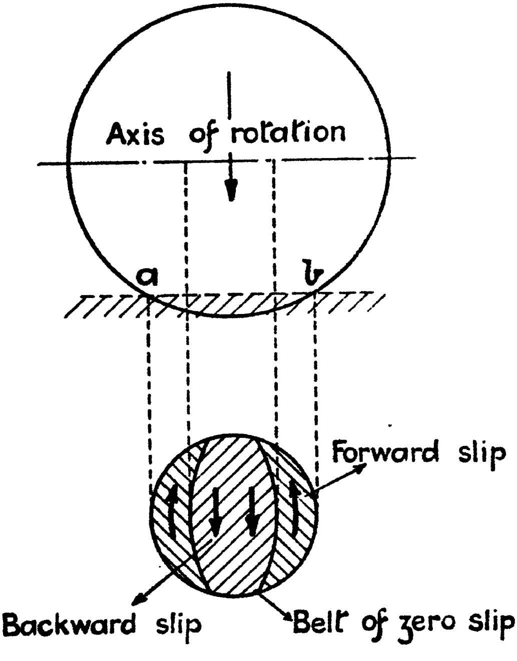
* Proc. Inst. Auto. Eng. xv.

by Heathcote. The rolling action in case C is therefore not pure rolling such as occurs in case A, and there is an additional source of friction present which will tend to increase the measured coefficient of rolling friction above the theoretical value. In case B a similar effect is present, but probably to a less extent when a small cylinder rolls on a large one. Unfortunately this additional friction cannot be computed; but if we recognize its presence, the results of Table V. are in reasonable conformity with those indicated by the theory.

Fig. 6.



8. The expression $q\frac{A_0}{p}\frac{l}{e}$ for the coefficient of friction suggests, as previously remarked, that μ may be related to the elastic constants in some way. This possibility will now be examined more closely. Consider, for simplicity, a sphere of one material A sliding on a plane of another material B to which we can apply Hertz's equations for elastic deformation. In the present theory, friction is supposed to be proportional to the number of molecules undergoing repulsion, and at the same time this number is supposed to

be proportional to the load, these suppositions leading to agreement with the well-known fundamental law of friction.

For a load F and radius r, Hertz shows that the contact circle has an area

$$\alpha \propto \mathrm{F}^{\frac{2}{3}} r^{\frac{2}{3}} (\vartheta_\mathrm{A}+\vartheta_\mathrm{B})^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

As we are at present only concerned with the nature of the material, we shall in the first place simplify the reasoning by regarding F and r as constant, under which conditions

$$\alpha \propto (\vartheta_\mathrm{A}+\vartheta_\mathrm{B})^{\frac{2}{3}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

In the theory it is assumed that

$$\mathrm{F} = n\bar{p},$$

and in the case of a soft material the maximum repulsion between two molecules will be small, not because the molecules are incapable of exerting greater repulsion, but rather because the lattice strength will not support any greater force without distortion. Hence for the soft material the mean repulsion $\bar{p}$ will also be small, and to support the load F the number of molecules must be correspondingly large. In terms of elasticity the more yielding material has a high value of ϑ and a large contact area α.

For the given load F the value of n is inversely proportional to $\bar{p}$. But the coefficient of friction by equation (2) should also be inversely proportional to $\bar{p}$ and therefore directly proportional to n, where different materials are concerned, or, substituting in equation (2),

$$\mu = \frac{q\mathrm{A}_0\bar{l}n}{\mathrm{F}e}.$$

If, as we may reasonably assume, there is some simple relation for various materials between the molecular quantity n and the elastic quantity α, we may write n as some function of a, let us say $f\,(a)$.

Hence $$\mu \propto \frac{q\mathrm{A}_0\bar{l}}{\mathrm{F}e}\, f\,(\vartheta_\mathrm{A}+\vartheta_\mathrm{B})^{\frac{2}{3}},$$

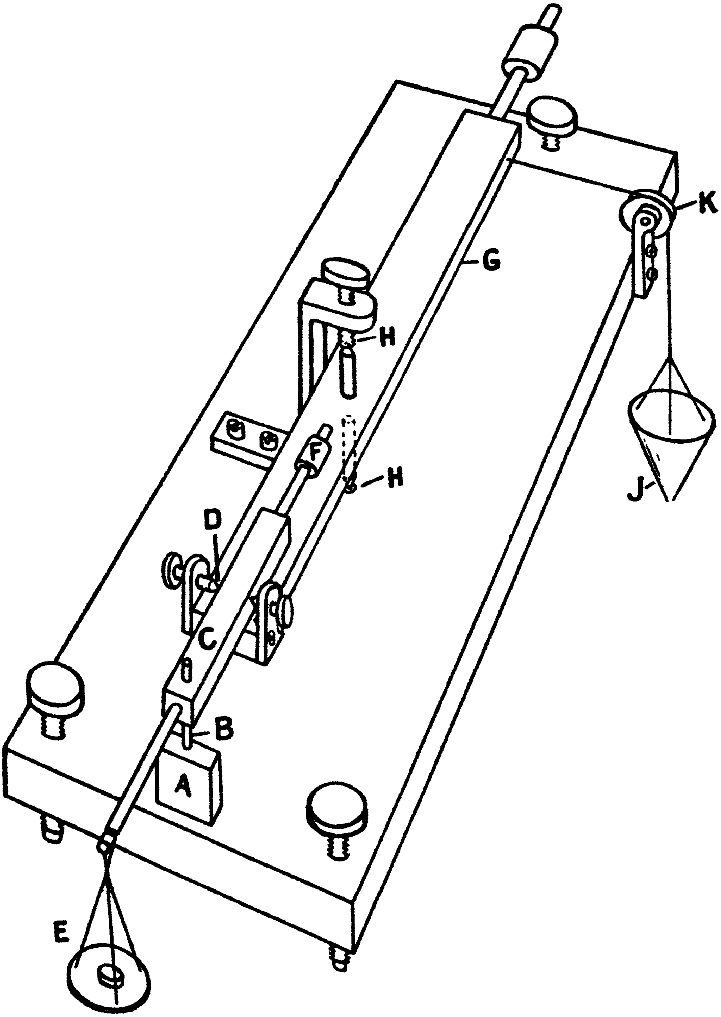
and we may therefore expect to find some systematic connexion between μ and $(\vartheta_\mathrm{A}+\vartheta_\mathrm{B})^{\frac{2}{3}}$. It has actually been found from the measurement of a large number of coefficients of friction that μ is directly proportional to $(\vartheta_\mathrm{A}+\mathrm{B})^{\frac{2}{3}}$ with a fair degree of exactness.

Before describing these experiments we shall briefly consider the meaning of this experimental result. It follows in general that the harder the two materials are the smaller the coefficient of friction will be. Also, since in the present argument F is a constant and q may be assumed to have a similar value for any material, the quantity $\frac{A_0\bar{l}}{e}$ can be regarded as the same for all the different materials used. The atomic distance e does not vary greatly amongst the different metals; hence $A_0\bar{l}$, which represents the loss of energy in a single molecular separation, is roughly constant. This deduction appears to be not illogical on general grounds, for when the molecular cohesion bond is weak, that is A_0 is small, one would expect the displacement of the molecule beyond its limiting stable position to be greater.

The available data on dry friction were found to be somewhat meagre; and as this relation has a very important bearing on the present theory, a fairly extensive series of coefficients of friction has been measured. In this series ten different materials were used in all the possible combinations, yielding altogether 55 different coefficients of friction. The apparatus used for the purpose is shown by a perspective sketch in fig. 7. A plane surface A of one of the two materials has a spherical end B of a rod of the other material in sliding contact with it. The rod is carried by a lever C pivoted about a horizontal axis on hardened steel points D. A light scale-pan E is suspended from the free end of this lever, and the whole can be balanced by a counterpoise weight F. The supports for the pivot are themselves attached to a second lever G, which is similarly pivoted about a vertical axis on points H. A known normal load can be applied by weights in the pan E, and the tangential friction force is applied by feeding a fine stream of silver sand into a paper hopper J, which is attached to the lever G by a thread of cotton passing over a light pulley K. The effect of the friction of the various pivots on the results was found to be quite negligible, all the pivots being carefully prepared on a special pivot lapping machine in use at the National Physical Laboratory. The apparatus can be balanced and levelled so that the lever G floats freely in any position.

The contact surfaces, when of metal, were worked up on the finest grade of blue-black emery paper and finally polished on wet chamois leather. The surface was washed with a cleaning fluid and scrubbed with a pad of specially pure cotton-wool until a clinging contact was obtained and the surface emitted a continuous squeaking noise under the motion of the pad. In the case of lead the surfaces could not be polished and cleaned in the above way, and cleanness was ensured by working with a freshly-cut surface of the metal, prepared by paring it with a clean razor blade. With glass a fused spherical slider and a piece of plate glass were used.

Fig. 7.



The measured coefficients of friction are given in Table VI., and in Table VII. the computed values of the ratio

$$\frac{(\vartheta_A+\vartheta_B)^{\frac{2}{3}}}{\mu}\times 10^8$$

are given. An inspection of Table VII. shows this ratio to be nearly constant. The mean value is $5{\cdot}47\times 10^{-8}$, and 42 of the 55 values lie within about 10 per cent. of the mean. If the mean value of the ratio is found for each material when paired in turn with all the materials, the constancy is even more striking. These mean values are shown in the last row.

The experimental results thus show that the coefficient of friction of any two surfaces is not a fortuitous constant, but is a function of the elastic moduli K and C, and may be expressed with a fair degree of accuracy by an equation,

$$\mu=0{\cdot}18\times 10^8\,(\vartheta_A+\vartheta_B)^{\frac{2}{3}}.$$

As regards their bearing on the theory of friction, these results certainly appear to support the assumption that the number of molecules in repulsion adjusts itself to be proportional to the load, and that the friction is proportional to this number. It should be made clear that, although the coefficient of friction is found proportional to the contact area in the restricted case of equation (14), it is not to be understood that this applies in the general case of equation (13). In other words, the number of molecules in contact is not proportional to the total area, the number per unit area being a function of the radius of curvature and of the actual load applied, as might be expected, since the intensity of normal stress depends on these variables.

The series of coefficients of friction in Table VI. is in itself of some interest. It will be seen that the values found for any one material taken in turn with all of the materials are in ascending order of magnitude, which is the same for every material. Also, where any two materials A and B are concerned, the coefficient μ_{ab} is nearly always intermediate between μ_{aa} and μ_{bb}. These results of course follow at once from the more general relation,

$$\mu\propto(\vartheta_A+\vartheta_B)^{\frac{2}{3}}.$$

9. There is no theory of sliding friction which has general acceptance, but in the case of rolling friction a theory was developed by Osborne Reynolds * which has been considered

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* Phil. Trans. Roy. Soc. lxvi.

TABLE VI.

	Hard steel.	Mild steel.	Platinum.	Nickel.	Copper.	Brass.	Aluminium.	Glass.	Tin.	Lead.
Hard steel ……	·393	·410	·398	·428	·548	·535	·649	·605	·785	1·955
Mild steel………	·410	·411	·427	·429	·533	·506	·605	·721	·786	1·930
Platinum ………	·398	·427	·445	·386	·592	·560	·796	·569	·855	2·070
Nickel ……….	·428	·429	·386	·389	·562	·504	·745	·775	·895	2·150
Copper …………	·548	·533	·592	·562	·600	·618	·695	675	·857	1·945
Brass ………	·535	·508	·560	·504	·618	·634	·706	·873	·752	2·110
Aluminium .. …	·649	·605	·796	·745	·695	·706	·937	·845	·905	2·000
Glass …………	·605	·721	·569	·775	·675	·873	·845	·940	·941	2·420
Tin ……… … ..	·786	·786	·855	·895	·857	·752	·905	·941	1·110	2·250
Lead ……………	1·955	1·930	2·070	2·150	1·945	2·110	2·000	2·420	2·250	3·310

TABLE VII.

	Hard steel.	Mild steel.	Platinum.	Nickel.	Copper.	Brass.	Aluminium.	Glass.	Tin.	Lead.	C dynes per sq. cm.	K dynes per sq. cm.
Hard steel…	5·55	5·47	5·97	5·32	5·20	5·71	5·28	6·12	5·19	5·23	8·9 × 10¹¹	18·0 × 10¹¹
Mild steel .	5·47	5·64	5·69	5·44	5·43	6·14	5·89	5·20	5·29	5·36	8·1	16·4
Platinum ..	5·97	5·69	5·70	6·29	5·09	5·73	4·58	5·56	4·94	5·02	6·1	24·7
Nickel ……	5·32	5·44	6·29	6·03	5·18	6·19	4·81	4·85	4·63	4·81	7·7	17·6
Copper .. …	5·20	5·43	5·09	5·18	5·79	5·88	5·80	6·24	5·35	5·44	4·0	13·6
Brass …..	5·71	6·14	5·73	6·19	5·88	6·02	5·98	5·03	6·02	5·10	3·5	10·6
Aluminium .	5·38	5·89	4·58	4·81	5·80	5·98	4·94	5·65	5·65	5·51	2·7	7·5
Glass …..	6·12	5·20	5·56	4·85	6·24	5·03	5·65	5·24	5·61	4·60	2·9	4·0
Tin ………	4·19	5·29	4·94	4·63	5·35	6·02	5·65	5·61	5·06	5·10	2·05	5·3
Lead ……	5·23	5·36	5·02	4·81	5·44	5·10	5·51	4·60	5·10	4·78	0·34	5·0
Mean values.	5·51	5·56	5·57	5·37	5·54	5·78	5·42	5·52	5·29	5·11		

adequate for many years. In the present paper no distinction is made between rolling and sliding friction, both being supposed to arise in the same molecular plucking action. In thus proposing an alternative theory of rolling friction, we are obliged to inquire whether there are any reasons for considering Reynolds's theory inadequate, especially in view of the established character of this theory and the eminence of its author.

According to Reynolds's theory, rolling friction is caused by slight relative tangential motion between the surfaces in contact, due to unequal elastic surface displacements. There is supposed to be a differential creep motion in continuous operation, and this theory thus reduces rolling friction to a particular case of sliding friction. There can be little doubt that this kind of elastic creep does in general occur, with a contribution to the total loss of energy depending on the amount of load. It is the writer's opinion, however, that the amount of this rubbing motion is much too minute to account for more than a small part of the energy lost in rolling, and that this loss is mainly the result of the molecular disturbances which take place on account of the continual shifting of the loaded area. It may be observed that Reynolds's theory is purely descriptive and has never been applied quantitatively, and no criticism as to the accuracy of Reynolds's deductions is now suggested other than modifying the accepted idea of the magnitude of the creep effect and regarding it as only a small contributary cause of friction.

Several reasons can be adduced showing the elastic creep theory to be inadequate. In the first place, reference must be made to some experiments made by the writer at the National Physical Laboratory in connexion with an investigation on rusting of steel surfaces in contact *. It is very well known that when two steel surfaces in close contact have a relative sliding motion, the surfaces become pitted and a brown oxidation product is formed. The same result is found when the surfaces are held tightly together if they are subject to vibration. In this case the only motion occurring is the minute amount due to vibration. In the course of this research it was found that a relative motion as small as 8×10^{-8} inch was quite sufficient to cause rusting. On the other hand, it was found that a prolonged rolling motion never led to any formation of rust at all. We may therefore infer that the differential surface motion in rolling is less

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* Proc. Roy. Soc. p. 472 (1927).

than this very small amount. This can be verified by a simple approximate calculation. Taking the case of rolling given in Table I., we can form an estimate of the magnitude of the surface displacement in the contact area. Love[*] gives an illustration of the lines of principal stress in the neighbourhood of an elastic contact, which shows that the tangential stress over the surface in contact is a compressive stress which changes to a tensile stress on crossing the border of the contact area. It is therefore zero at the edge of the contact area, and the average will be smaller than the maximum. Let us assume that the average tangential elastic strain is 0·001; then the displacement of the edge of the contact strip relative to the centre is

$$4{\cdot}14\times10^{-4}\times0{\cdot}001 \text{ cm.}$$

or

$$16{\cdot}3\times10^{-8} \text{ inch.}$$

We are only concerned in Reynolds's theory with the differential displacement of the two surfaces, which must be considerably smaller than the above value of the total displacement; hence the calculation roughly bears out the inference from the experiment, that the differential creep does not exceed about 8×10^{-8} inch. Further, the elastic creep is not uniform, but varies between zero and a maximum value at different parts of the contact surface, so that the average creep which is supposed to produce the friction must be a still smaller quantity. It is difficult to understand how such extremely minute relative movement can cause the loss of energy found in rolling, and the difficulty is increased by the fact that the coefficient of sliding friction undergoes a marked diminution at such small amplitudes, as we have shown in section 6.

There are two further arguments which show that Reynolds's theory does not fully account for rolling friction. The first is based on the fact that the coefficient of rolling friction is inversely proportional to the width of the contact area which is demonstrated by both Goodman's and the author's experiments. On Reynolds's theory it appears to be quite impossible to account for this result without arriving at some untenable conclusion as to the relation between the slip and the width of the contact strip. Since the coefficient is known to decrease when the load is increased, it follows that the amount of differential creep in rolling any given distance must decrease when the load is increased. The width of the contact increases with the load in a definite manner;

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[*] 'The Mathematical Theory of Elasticity,' p. 196.

hence we should be forced to the difficult conclusion that the creep decreases as the total arc of contact increases.

The second argument is a simple one. Consider the case of two identical parallel cylinders, one rolling upon the other. In such a case we have perfect symmetry, and the elastic distortions of the two bodies will be exactly alike and the friction in this particular case should on Reynolds's theory be zero, or at least abnormally low, or, if not, some other explanation of the friction must be found. This interesting point was tested by experiment, and the coefficient of friction was determined for parallel cylinders of equal diameter. the lower being stationary with the upper one rolling to and fro upon it. With an amplitude of 0·0188 radian the coefficient was found to be 0·000022, and for direct comparison the friction was then measured after replacing the lower cylinder by a plane surface of the same material and having the same length of contact parallel to the axis of rolling. In the latter experiment with the same amplitude of rolling, the coefficient of friction was found to be 0·000034. The experiment thus shows that the rolling friction of two equal parallel cylinders is not at all exceptionally small, and must arise in some other way than that suggested by Reynolds. It may be remarked that the molecular theory now suggested also offers a simple explanation of the phenomenon described by Reynolds of the oscillation of a roller lying on a plane, if the roller is slightly disturbed. The molecular attractions which the theory supposes are clearly unsymmetrical after a small displacement, and give the resultant restoring couple necessary for an oscillatory rocking motion.

10. One interesting consequence of the molecular theory of friction may be noticed—namely, that by this theory a small loss of energy occurs when two bodies touch with any pressure and separate again in a direction normal to the surfaces; or, in other words, there is some "friction" with purely normal action.

Sir William Hardy has drawn attention to the possibility of this [*], but he states that no friction has been detected with normal motion. The loss of energy involved by the present theory is, in fact, so small as to be imperceptible. It can be easily computed as follows. Let the normal pressure exerted be F; then, using the previous notation,

$$F = n\bar{p},$$

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[*] Proc. Roy. Soc. c. (1922).

and the loss of energy is

$$E = n \times A_0\bar{l}$$

$$= \frac{FA_0\bar{l}}{\bar{p}}. \qquad \qquad (15)$$

Using equation (2), this becomes

$$E = \frac{\mu Fe}{q}.$$

Thus the loss of energy is proportional to the pressure, and is equal to the work done when the applied force is exerted through a distance $\frac{\mu e,}{q}$ an amount comparable with though probably less than the dimensions of the molecules. It is thus not surprising that this loss of energy, if it actually occurs, has not been observed, except as manifested, according to the present theory, in the case of rolling friction, which may be regarded as a continuous process of normal approach and recess.

11. It was remarked in section 1 that when two molecules of actual bodies come into repelling contact and then separate, each molecule has a strong bias to return to its parent body, although momentarily the two are supposed to be in similar equilibrium to that existing within the body of the solid. We shall now discuss this in more detail. The experiments, already referred to, made by the writer on the contact rusting of steel pointed to the conclusion that molecules are torn away by cohesive attraction, and such molecules have a strong affinity for oxygen molecules, the combination giving rise to the brown deposits observed. There is thus definite reason to believe that some of the molecules concerned in contact are detached, and this may be the mechanism of wear.

It can be shown, however, from our knowledge of the ordinary rate of wear of metals, that only a very small proportion of the molecules can be detached.

Each molecule taking part in contact dissipates an amount of energy of average value

$$A_0\bar{l}.$$

And the mass of the molecule for the present purpose is given closely enough by

$$m = \rho e^3, \qquad \qquad (16)$$

where ρ is the specific gravity and e is the distance between the molecules.

In dissipating energy in friction of amount E ergs, the number of molecular contacts is therefore

$$N = \frac{E}{A_0 \bar{l}} . \quad . \quad . \quad . \qquad (17)$$

And the mass of all the molecules involved is

$$M = Nm = \frac{E\rho e^3}{A_0 l} \quad . \quad . \quad . \quad . \qquad (18)$$

From equation (2) we can substitute

$$A_0 \bar{l} = \frac{\mu}{q} \bar{p} e.$$

Whence

$$M = \frac{E\rho e^2 q}{\mu \bar{p}} . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

In this expression $\bar{p}$ is unknown and q is of the order of unity, but is otherwise unknown. If, therefore, we can in any way arrive at some reasonable estimate of $\bar{p}$ and take q as unity, we shall obtain a probable value for the value of M.

The experiments made by Stott on pivots, already referred to, show that a material has a definite flow-stress and is not capable of supporting any stress exceeding this. Mallock * and Hankins † have also independently found somewhat similar results. It will be assumed that this state of flow indicates a condition in which all the available molecules are repelling with the maximum possible force, that is, the limiting force the space-lattice can resist.

If the flow-stress is denoted by f, we then have approximately

$$f = \frac{p_{\max}}{e^2}.$$

In a case of elastic contact $\bar{p}$ will be smaller than $p_{\max.}$, and if we assume all the possible values of p to be equally probably, $\bar{p}$ will be equal to $\frac{1}{2} p_{\max}$.

By taking q as unity, this leads to the following expression for the value of M:

$$M = \frac{2E\rho}{\mu f} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

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* 'Nature,' cxvii.

† Proc. Inst. Mech. Eng. (1925).

The value of f found for unhardened steel by Stott is about 250 kilogrammes per square millimetre, and a concrete example will best show that the calculated value of M is very large.

If we consider, for example, a brake horse-power test of a 100 KW. motor dissipating this power for 1 hour by means of a brake on a steel flywheel, then the value of M is of the order 10^7 gram. The actual weight of metal which would be worn away is probably only some small fraction of a gram. Thus, although some very free approximations have been necessary in the above computation, we may quite safely conclude that only an extremely small proportion of those atoms taking part in contact are detached from their original position.

This suggests as an interesting possibility that wear may be fundamentally only an accidental accompaniment of friction. For the purpose of providing an illustration, let us assume the actual wear in the above example to be as much as 1 gram. We may anticipate by remarking that quite a large error in this conjecture does not materially affect the conclusions. On this assumption, only 1 in 10^7 of the molecules effective in causing friction is detached. The total number of molecules which come into contact is

$$\mathrm{N}=\frac{\mathrm{M}}{m}=\frac{2\mathrm{E}}{\mu f e^3}. \quad \ldots\ldots \quad (21)$$

Taking e to be $2{\cdot}86\times10^{-8}$ cm., this has a value of about 5×10^{28}, so that the number detached, although only a very small fraction of this, is still a very large number of the order 5×10^{21}. Hence, as in many molecular phenomena, although the wear may be ultimately traceable to the accidental loss of an occasional molecule, the total number involved is so great that uniformity and consistency are always found in the results perceived by measurement.

12. In the course of the experimental work some unusual cases of friction have been encountered which appear to deserve a brief mention. These are instances in which the cohesive attraction of the surface atoms is not negligibly small by comparison with the external force applied between the surfaces in contact. Consequently the normal reaction between the bodies is considerably greater than the applied force, and extraordinary values are obtained for the coefficient of friction, as usually defined.

In one experiment a light slider was used having 3 feet of lead forming an equilateral triangle. The slider was placed on a clean piece of plate glass which could be tilted to any angle. To obtain clean surfaces of lead, the 3 feet were pared away with a clean razor blade. The glass surface and the blade were cleaned by repeated rubbing with a mixture of alcohol, ether, and ammonia. It was found that the plate could then be tilted completely into the vertical position without any slipping of the slider, giving an infinite coefficient of friction by the ordinary definition. Further, with a little care, it was found possible to turn the glass plate round until it was horizontal with the slider in its original position clinging to the under side, showing that the cohesive attraction could exceed the weight of the slider.

Similar results were obtained with two fibres of quartz or glass crossed at right angles. In this case strong cohesive forces can be observed and measured by the elastic deflexion of the fibre, and tangential frictional forces were measured when the applied normal force was zero or even negative, leading to a series of apparent coefficients of friction passing through infinity to negative values.

These experiments illustrate clearly that the coefficient of friction should be defined in terms of the normal reaction between the bodies, rather than in terms of the applied normal force. Otherwise, under certain circumstances, the friction will be far from proportional to the load, and very abnormal values of the coefficient will be obtained.

13. We shall conclude this paper with a short discussion of the fundamental hypothesis that has been assumed concerning the character of the atomic forces of attraction and repulsion. It has been seen in the course of the paper how the various experimental results support the deductions from the theory, even when the theory has indicated certain relations not hitherto recognized, such as the relation between friction and the elastic constants or the relation between sliding and rolling friction. The validity of the theory, however, depends so much on the simple assumption that the repulsion has a much greater rate of change and a smaller range of action than the attraction, that we shall attempt to show in a simple way how the same hypothesis is consistent with the ordinary phenomena of elasticity. A number of writers have dealt mathematically with the connexion between elasticity and atomic forces, but a

varied from normal by two-fold dilutions down to $n/10000$. In all dilute solutions the anomalous effect looked for was noticeable, and most marked in concentrations from $n/500$ to $n/1000$. It was further ascertained that the maxima occurred whether slowly- or quickly-dropping capillaries were used, or ordinary or extraordinary purity of reagents and distilled water were employed. The character of this anomaly remained the same no matter whether freshly-prepared solutions were used or old ones long standing with mercury. The suggestion of Prof. Kučera that this secondary maximum may be due to traces of mercury coming into solution by oxidation on contact with air was carefully investigated by Dr. Rasch (4), who found that this explanation cannot hold: addition of mercuric oxide or mercurous salts to the solution caused only unimportant changes at the beginning of the electro-capillary curves, and no difference in the anomaly was found whether anions forming insoluble salts with mercury (*e.g.*, chlorides, hydroxides, iodides) or soluble ones (nitrates) were present in the solution *.

The influence of the increase or decrease of the applied E.M.F. upon the potential at which the discontinuous fall of the interfacial tension occurred was closely investigated in the case of $n/1000$ sulphuric acid. No marked difference could be detected whether we approached the maximum from higher or lower voltages, it always occurred at 0·96 volt of polarization. The same solution as standing in a beaker open to the air has now been investigated polarographically, which method elucidated at once the nature of the Kučera anomaly.

Concerning this method little will be mentioned here, since it has been fully described recently in numerous communications (5). The method consists in the investigation of current-voltage polarization curves, now registered automatically by means of a special photo-registering apparatus, the polarograph †. The polarizing voltage is plotted as abscissa against the corresponding current, the curve being drawn on a rotated photographic paper by a beam of light reflected from the mirror of a sensitive galvanometer.

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* For the entirely different type of polarization curves with solutions containing mercury salts, see the recent paper of P. Herasymenko, J. Heyrovský, and K. Tančakivský, "Maxima on Current-Voltage Curves.—Part III. The Electrolysis of Mercury Salts Solutions with Dropping and Steady Mercury Cathodes." Trans. Faraday Soc. xxv. p. 152 (1929).

† The apparatus used lately was constructed by the firm, Dr. V. Nejedlý, Prague, Radešovice, No. 92.

Qualitative and quantitative deductions are made from the increase of current occurring at various potentials about reducible matters dissolved in the electrolyte solution. Hitherto all solutions to be investigated were carefully freed from air by bubbling hydrogen through them in order to avoid the great increase of current due to the reduction of atmospheric oxygen.

The polarographic curve obtained by electrolysing the $n/1000$ sulphuric acid solution in the same beaker exposed to the air, and using the same capillary of the mercury-dropping cathode with all experimental conditions unchanged, revealed a very sharp maximum (see fig. 2) of the current falling discontinuously at 0·96 volt, *i. e.*, at the same voltage as on the electro-capillary curve. It at once became evident that this polarographic maximum, just as the electro-capillary one, can only be due to the atmospheric oxygen dissolved in the solution. The increase of current on air shows by its magnitude (after the maximum) that the reducible matter is present in a concentration of ca. 0·0012 gram equivalent per litre, which corresponds to the concentration of atmospheric oxygen dissolved in aqueous solutions at room temperature. Further, the increase of current starting from the beginning of polarization proves that the matter in solution is an easily reducible substance. To demonstrate this action of oxygen beyond doubt, the oxygen content in solutions was changed, its partial pressure being varied from zero to one atmosphere. In all cases the electro-capillary and polarographic curves were determined. The special electrolytic vessel used in this investigation is shown in fig. 3. In this arrangement first pure hydrogen was passed through the solution of a dilute electrolyte ($n/1000$ H_2SO_4 or $n/100$ KCl) contained in the wash-bottle *a*, electrolysing vessel *b*, and the beaker *c*, in which it was covered by a layer of paraffin-oil. After four hours' bubbling the current of hydrogen was stopped and the electro-capillary parabola obtained by collecting the polarized mercury drops in the glass spoon *d* and weighing. In this way Kučera's method could be applied without the intervention of the atmospheric oxygen. The resulting curve was a smooth parabola (see fig. 4), No. 1, devoid of any anomalies. Next, the same solution was investigated polarographically under exactly identical conditions of polarization. The horizontal line thus registered (see fig. 5) showed that in this solution no trace of reducible matter is contained. Next, oxygen (from a cylinder) was passed through the solution for several hours, and both the polarographic as well as the electro-capillary curves were obtained; the polarogram showed a curve similar to that of No. 4 (fig. 6), which exhibited a marked maximum and a residual current almost five times as great as observable on the curve belonging to the solution standing open on air (compare fig. 6, curve 3). The electro-capillary parabola was much deformed, showing a prominent secondary maximum with a discontinuous fall, much more marked than when obtained with air. The position of the discontinuous fall of the electro-capillary parabola occurring in this solution at 1·34 volt coincided exactly with the voltage of the discontinuous fall on the polarographic curve. From these and similar investigations it became evident that the sudden change of current at the maximum is always accompanied by a sudden change of the interfacial tension of mercury, *i.e.*, by Kučera's anomaly. In view of the

Fig. 3.

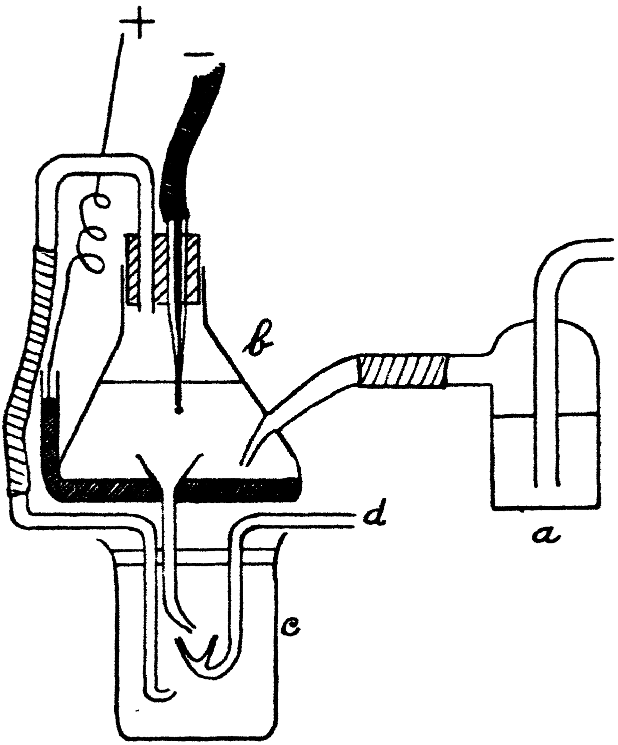
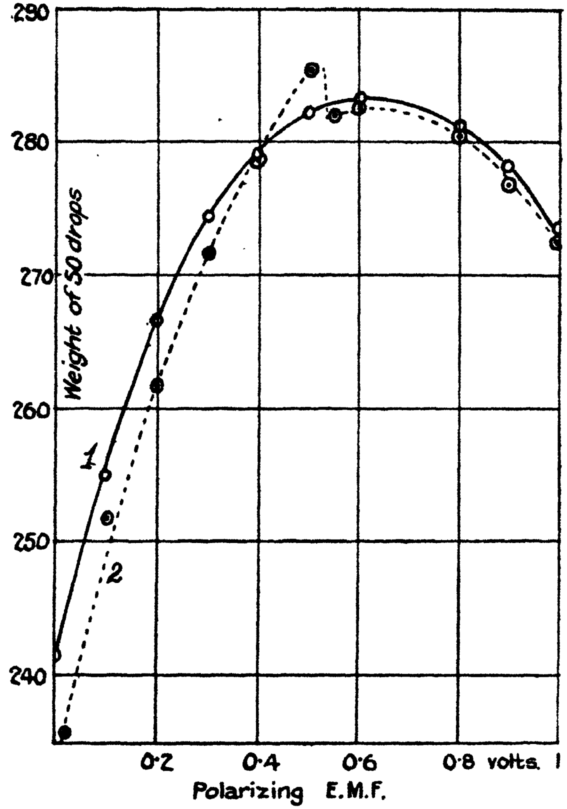
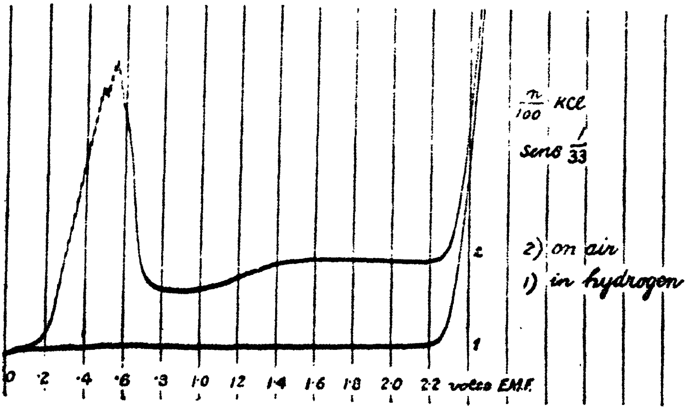


Fig. 4.



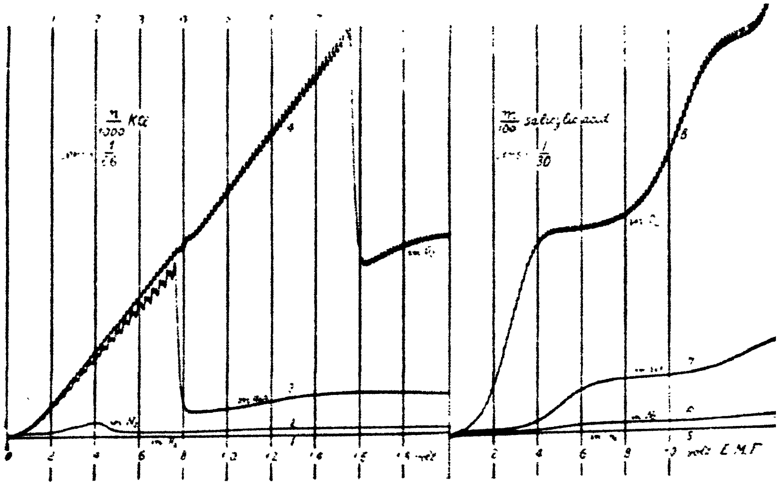
(1) *n*/100 KCl in the atmosphere of hydrogen.
(2) Open to air.

Fig. 5.



experimental difficulties and the slow procedure of the drop-weight method, further investigations on the nature of the anomalies were carried out by the polarographic method only, the parallelism between the two phenomena being taken as certain. Thus one curve could be obtained in 10 minutes polarographically, *i. e.*, automatically, whereas the electro-capillary method required 4 hours of tedious counting of drops and weighing before these results could be plotted on the curve. Moreover, the disturbing influences are much more pronounced on the current-voltage curve than on the electro-capillary one, and the electrolytic changes, which are no doubt here displayed, are far more precisely defined by the intensity of current than by the drop-weight method.

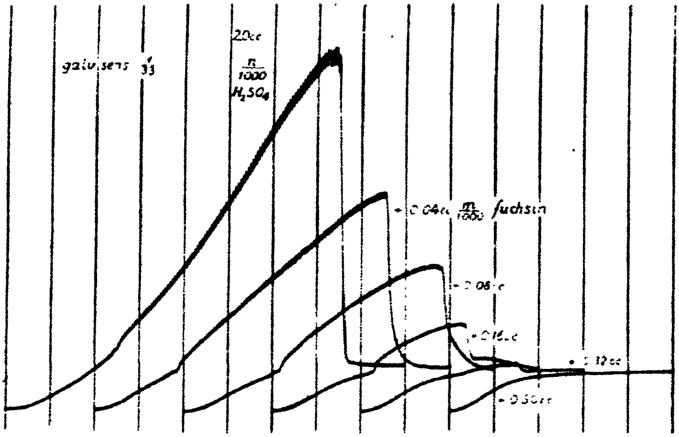
Fig. 6.



Thus, to find polarographically in which concentration the anomaly is most prominent, a series of measurements was made while increasing the concentration of sulphuric acid exposed to air in the electrolytic vessel, *i. e.*, the electrolyte being saturated by the partial pressure of atmospheric oxygen. This polarogram (fig. 2) shows that the highest maximum is reached in a milli-normal solution, which coincides precisely with the previous experience. Much attention is now paid to the conditions of occurrence of the highest maximum by the work of several collaborators (Rasch, Varasová, Dillinger). It has been ascertained that the highest maximum always occurs in a milli-normal solution of any strong electrolyte. In solutions of weak electrolytes the concentration has to be increased so as to produce an ionic concentration ca. milli-normal; such results, arrived at by Dr. Rasch in this laboratory, coincide again with the facts described by Prof. Kučera in his communication on the appearance of the electro-capillary anomalies in aqueous solutions of fatty acids[8]. Both highest maxima occur here in normalities of $n/10$ to $n/20$, which contain an ionic concentration about milli-normal.

This concentration applies only to the solubility of atmospheric oxygen. If these solutions are saturated by pure oxygen under atmospheric pressure, the electrolyte in which the highest maximum is developed has to be ca. five times millinormal.

Fig. 7.

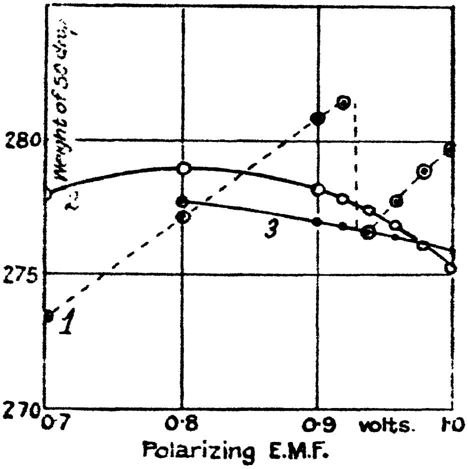


Since previous investigations on maxima on polarographic curves have shown the suppressive effect of various electrolytes and non-electrolytes, a similar influence was expected on maxima due to oxygen. The results show that concentrations of strong electrolytes increasing above milli-normal almost equally suppress the maximum (compare Herasymenko, *l.c.*), and that one of the most active matters in this respect, viz. fuchsin (compare Emeljanová and Heyrovský, *l.c.*) was equally powerful in suppressing the maxima due to oxygen. The polarogram (fig. 7) shows this marked effect of fuchsin, where already 1/2 c.c. of a milli-molar solution of fuchsin hydrochloride added to 20 c.c. of a milli-normal sulphuric acid suffice to remove the phenomenon of maximum entirely.

Hence it was concluded that the presence of this substance equally removes Kučera's anomaly; indeed, the electrocapillary curve (fig. 8) obtained with the same fuchsin solution open to air gave a smooth apex of a parabola without the anomaly.

The next experiments were of a quantitative nature to investigate how far the electrolytic current can indicate the content of oxygen in solution. The polarogram (fig. 6) represents the result of this investigation. The lowest horizontal line (curve 1) is the current voltage curve of a milli-molar solution of potassium chloride from which the air has been driven out by hydrogen. The next curve (No. 2) has been obtained from the same potassium-chloride solution saturated by commercial nitrogen on bubbling through it the gas from a cylinder for several hours. For the third curve the same solution has been standing open to air, whilst for the fourth the solution was saturated by commercial oxygen passing through it from a cylinder. When taking the percentage of oxygen in air as 21 per cent., the saturation currents after the maximum are in relation 0 : 3·5 : 21 : 91, showing the amount of oxygen dissolved in solution from the absorbed gases, viz. pure hydrogen, commercial nitrogen, air, commercial oxygen. An analysis kindly carried out by

Fig. 8.



$n/1000\ H_2SO_4$.

(1) In air. (2) In hydrogen. (3) Air with added fuchsin.

Prof. Sv̌éda in the Institute for Analytical Chemistry gives for nitrogen gas in the cylinder 2·83 per cent. and for oxygen gas 93·7 per cent.

Since such quantitative determinations are derived only from the magnitude of the saturation current, the maximum has to be suppressed in order to enable us to compare the total currents. This is easily done by using an aromatic derivative as electrolyte, as, *e.g.*, a centimolar solution of salicylic acid in fig. 6. Curves 5, 6, 8, and 7 were obtained from solutions saturated by the same stream of hydrogen, commercial nitrogen, and oxygen, or standing open to air, just as the curves 1, 2, 4, and 3, their currents increase again in the ratio 0 : 3·5 : 21 : 91, which indicates the oxygen content in the corresponding solutions.

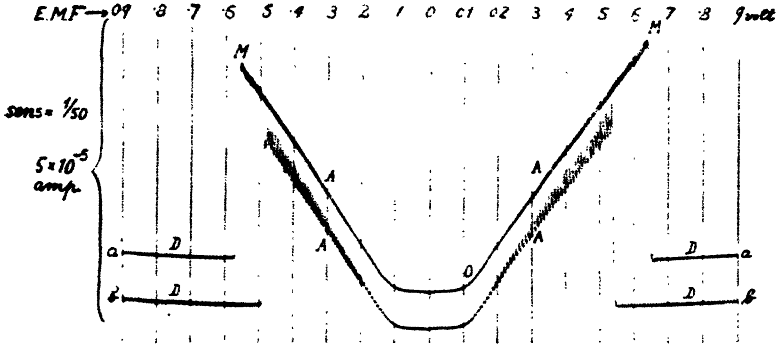
The calculation of the absolute content of oxygen in these solutions has been derived in the following manner:—The magnitude of the saturation current from curve 8 corresponds to 17·5 cm. of the galvanometer deflexion, where the sensitivity was 1/30—that means 525 cm. with the full sensitivity (1 : 1). Now in this arrangement a saturation current causing a deflexion 8 to 10 cm. is due to a concentration of the reducible matter in solution equal to 10^{-4} gr. equiv. per litre. Hence the concentration of the reducible matter present in the solution—in our case commercial oxygen—must be equal to 525/9, *i.e.*, $58 . 10^{-4}$ gr. equiv. per litre, whereas from the curve No. 3 (fig. 6) the saturation current being 2 cm. high with a sensitivity of galvanometer 1/66 leads to a concentration of oxygen almost five times smaller, viz. $14 . 10^{-4}$ gr. equiv. per litre, which corresponds to the solubility of atmospheric oxygen. The exact determination of the solubility of pure oxygen in water under the pressure of one atmosphere at the temperature of 16° C is (according to L. W. Winkler, Landolt-Börnstein tables) 0·04903 gr. per litre, *i.e.*, 0·0061 gr. equiv. Consequently, the solubility of atmospheric oxygen in water, the partial pressure of which is equal to 0·21 atm., is $13 . 10^{-4}$ gr. equiv. These numbers coincide with the above results, a similar agreement being found from saturation currents of any curve provided the concentration of the electrolyte in solution is not great

It is interesting to note that on curve 8 the reduction process of oxygen proceeds distinctly in two stages. Special investigations described elsewhere (9) have revealed that the first process consists in reducing oxygen to hydrogen peroxide; the next is due to the reduction of hydrogen peroxide to water. Each process requires the quantity of electricity 2 faradays per gram molecule of oxygen so that the total saturation current must correspond to a substance consuming 4 faradays per gram molecule, *i.e.* O_2, as was indeed just calculated.

Discussion of the Results.

The above experiments leave no doubt that it is directly the reduction of oxygen and not of its products in solution which causes the anomalous changes of electro-capillarity in the drop-weight method. It remains to explain the mechanism of this marked discontinuous effect. For this, the explanation of the occurrence of maxima on current-voltage curves has to be put forward as given by one of us recently (8). It has to be emphasized that such maxima occur in all reduction processes at the dropping mercury cathode whether inorganic or organic matter is deposited or reduced. In all such cases—whether these maxima occur round the potential of the calomel electrode or at a potential as negative as minus 2 volt, when indifferent electrolytes are added—the maxima become more rounded, and finally, with larger additions, suppressed still more so when complex organic compounds, even in mere traces, are present in the solution. No time-effects are observable with the duration of polarization. Further, the backwards polarization from 2 volts to zero gives a curve coinciding with the onwards polarization from zero to 2 volts, which is shown in fig. 9 *. Slight differences will be noted in this polarogram with the

Fig. 9.



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* The slight oscillations on the curves are caused by falling drops.

voltages at which the discontinuity occurs; these are discussed below as the "hysteresis" effect. It has to be mentioned that the change of external resistance, *e.g.*, galvanometer and shunt, has no effect upon the sharp shape of the maximum observable in ca. milli-normal electrolytes, even if varied from 1 ohm to 20,000 ohms. With larger resistances the slope of the ascending branch is considerably lowered, showing the electrolytic resistance in the cell in this case of the order of 20,000 ohms. The linear increase of the current (best seen in fig. 9, part A), well marked in very dilute solutions, permits us to calculate directly the internal electrolytic resistance of the cell. To an increase of the applied E.M.F. by 0·500 volt corresponds a linear increase of the current by $3{\cdot}45 \times 10^{-5}$ amp.; this is only possible when the cathode during this interval remains unpolarized and the electrolytic resistance equals $0{\cdot}500 : 3{\cdot}45 \times 10^{-5} = 15{,}000$ ohms. This value is to be expected from the specific resistance of the milli-normal electrolyte (ca. 10,000 ohms) when considering the shape and distance of the two mercury electrodes. Thus at the fall of the maximum the cathodic potential must at once increase by $\mathrm{R}\,.\,\Delta i = 15{,}000 \times$ (fall of current), which amounts to almost 0·50 volt. Henceforth (in part D) the cathode remains perfectly polarizable, as evident from the constancy of the current during further increase of the E.M.F. (compare(8), *l. c.* p. 264). The same influence of the electrolytic resistance upon the slope of the current is well observable in solutions of electrolytes below milli-normal (*e.g.*, fig. 2, curves 1, 2, 3). This slope, again, increases with the conductance of the solution, according to Ohm's law.

As to the position of the apex of maxima, it is observed that when increasing the concentration of reducible matter the maxima increase, and consequently the apex is shifted to more negative voltages. The increase of the rate of dropping shifts also the apex of a maximum towards a greater polarizing E.M.F.

This is well observable in fig 6, where the apex of the maximum due to pure oxygen (curve 4) occurs at the polarizing E.M.F. 1·550 volts, that due to the atmospheric oxygen (curve 3) at 0·760 volt, and that due to the oxygen content in nitrogen at 0·40 volt (curve 2). The other influence, viz. that of dropping, is visible from the polarogram 9, where curve *a* has been obtained with drops of 3·2 sec., and the curve *b* with drops of 6·7 sec. duration. This at once suggests that the phenomenon of maximum at the current-voltage curve, and with it Kučera's anomaly, will entirely disappear when using an infinitely slowly-dropping cathode, *i.e.*, a steady mercury surface as it is indeed observed at the smooth electro-capillary parabolas obtained by Lippmann's method, with the stable meniscus in the capillary electrometer.

The Rôle of Concentration-Polarization.

When recording the currents due to polarization of a small steady mercury cathode with the same anode and the same dilute electrolyte solution in which the prominent maxima with the dropping cathode are obtained, no reproducible maxima are observed unless the solution is well stirred. Thus stirring—whether effected by agitation of the solution around a steady electrode surface or by the continual drop formation at the dropping cathode—prevents the decrease of current. When stirring is applied, the decrease of current sets in only at great polarizing E.M.F., whereas with steady electrodes the current is known to diminish quickly at the beginning of the applied voltage. The latter phenomenon is well known to be due to concentration-polarization, *i. e.*, due to the formation of an exhausted layer of solution exhausted from reducible matter, through which layer the reducible matter only diffuses to the electrode, causing thus a small steady diffusion current. It is well known that this concentration-polarization may acquire considerable values, like those of concentration cells. Under the applied E.M.F. any steady electrode surface soon becomes a polarized "old" surface to be distinguished from the "fresh" one, maintained in the original concentration condition by the continual dropping of mercury or good stirring, in which case no concentration-polarization can start. This distinction between the "fresh" (*i. e.*, just being formed) and the "old" interface (*i. e.*, polarized by concentration-polarization) suffices to explain the phenomena of maxima.

Adsorption and Diffusion Currents.

The first consequence of the formation of an exhausted layer at any electrode is a total absence of any adsorption of the reducible matter, because now the interface is isolated from the bulk of the solution by the exhausted layer so that the adsorptive forces at the water-mercury interface cannot penetrate into the bulk concentration, being separated by a water film certainly thicker than 10^{-7} cm., which is regarded as the limit of the action of adsorptive (capillary) forces.

We thus may have the advantage of a positive adsorption of reducible matter at an electrode and of the consequent increase of current only when the concentration-polarization, *i. e.*, the formation of an exhausted layer, is totally prevented by perfect stirring. This is the advantage of the dropping mercury cathode with its fresh interface, which thus allows great currents aided by adsorption. However, this advantage of the adsorption of reducible matter is sustained only within a certain limit of the polarizing E.M.F., owing to the limitation of the rate of adsorption. Hence with increasing voltage the current increases maximally to the value when the rate of reduction of reducible matter is just equal to the rate of adsorption of the reducible matter to the interface; as soon as the rate of reduction exceeds the rate of adsorption, at once concentration-polarization must start at the mercury-solution interface; this removes adsorption entirely, and the current falls suddenly to the value maintained by the ordinary rate of diffusion of reducible matter through the exhausted layer to the electrode surface. The current due to voltages within that at which the maximum occurs (*e. g.*, fig. 9, parts A M) might be denoted as *the adsorption current* to be distinguished from *the diffusion current* occurring at voltages above that of maximum (fig. 9, part D).

It is also understandable why the concentration-polarization maintained at the dropping mercury cathode when polarizing with decreasing E.M.F. disappears at a smaller voltage (0·495 volt, curve *b*, fig. 9) than when increasing the E.M.F., in which case the discontinuity starts at 0·535 volt. This difference is, no doubt, due to the circumstance that it is easier to maintain the concentration-polarization, if once set up, than to start it if adsorption is displayed. In this explanation we have to imagine the concentration-polarization to be handed over from one drop to the other, which will be the more justifiable the slower the rate of dropping. As will be mentioned later on, small steady mercury cathodes exhibit also maxima, *i. e.*, adsorption and diffusion, currents, provided the solution is kept well stirred in air. When reversing the direction of the polarizing E.M.F. a similar hysteresis appears, but in much greater degree, which is understandable from the above principle of maintaining concentration-polarization when once started *.

The Cause of the Anomalies.

The explanation of the marked changes in the interfacial tension at voltages at which the maximum of the current occurs is now evident. Any sudden change in the polarization of a mercury cathode causes a corresponding change in the interfacial tension; if, now, the adsorption current changes into the diffusion current, and consequently great changes in the concentration at the interface as well as in the cathodic potential take place, the interfacial tension must accordingly be suddenly altered. Thus in the case of solutions electrolysed open to air, *i. e.*, containing atmospheric oxygen dissolved, the interfacial tension, when the applied E.M.F.'s still allow an adsorption current, is notably different from the interfacial tension due to polarizations at which the concentration-polarization is already established. The transition from the former to the later state of polarization is the cause of Kučera's anomalies. From this point of view it will be clear that in Lippmann's method of capillary electrometer no such anomalies can occur, since at this small stable mercury surface concentration-polarization starts from the very beginning of the polarizing E.M.F. In other words, Lippmann's mercury cathode is always an "old" perfectly polarized interface, widely different in conditions of polarization from those at the "fresh" interface of the dropping cathode at which adsorption phenomena are displayed. Our measurements show an increase of the interfacial tension mercury-solution $\gamma_{1,2}$ when the concentration of oxygen in solutions is increased, and a sudden fall in $\gamma_{1,2}$ when oxygen is—according to the above view—exhausted by concentration-polarization. The simple application of Gibbs's adsorption formula would lead one to expect the reverse—viz. a lowering of surface-tension by positive adsorption at the interface mercury-solution; however, it must be borne in mind that the changes of the interfacial tension $\gamma_{1,2}$ need not obey the simple thermodynamic deductions of Gibbs, which suppose conditions of surfaces chemically unchanged by adsorption. When oxygen comes into the interface, the physical conditions are there complicated (*e. g.*, by an alteration of the distance between the surfaces or the chemical action of O_2 or H_2O_2 at the interface) so that no exact formula is available for the calculation of $\gamma_{1,2}$ from the surface-tension of the solution γ_1, and from the surface-tension of mercury γ_2. Prof. Kučera used in his communication Neumann's formula,

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* For similar hysteresis phenomena accompanying maxima see the above cited paper of P. Herasymenko, J. Heyrovský, and K. Tančakiský.

$$\gamma_{1,2}=\gamma_1+\gamma_2-2\,A,$$

where A is the "adhesion" between the two phases, whilst, according to Antonoff, an empirical relationship might be applied:

$$\gamma_{1,2}=\gamma_2-\gamma_1.$$

The latter formula would show why $\gamma_{1,2}$ has to increase if adsorption of O_2 or H_2O_2 lowers γ_1 or increases γ_2; if Neumann's formula were valid, our results would mean that positive adsorption of oxygen at the interface mercury-solution largely diminishes the "adhesion" A between the two phases.

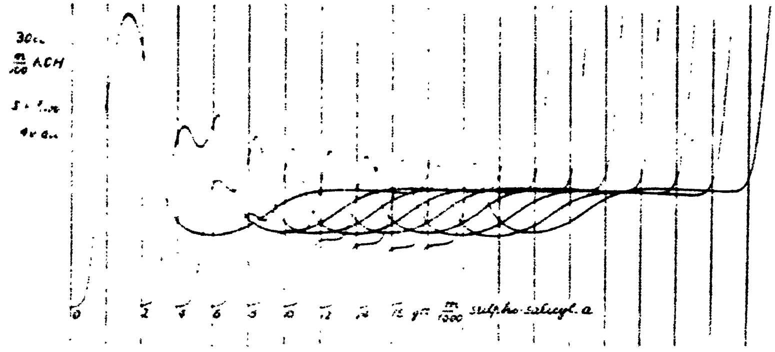
The curious phenomenon that the interfacial tension of mercury decreases when during electrolysis oxygen is removed, has no analogy in changes of interfacial tension observable in maxima due to other electro-reductions, *e.g.*, in solutions of mercury, thallium, nickel, uranyl-salts; it has thus to be ascribed to a chemical action of oxygen or its reduction product, the hydrogen peroxide, upon mercury.

The Suppressive Effects.

The suppressive effect of very dilute adsorbable matter upon the maxima is also easily understandable from the above point of view of adsorption at interfaces. Such substances as organic dyes (fuchsin, eosin, fluorescein, methylene blue, etc.) or aromatic compounds (like benzoic, salicylic, aceto-salicylic, sulpho-salicylic acids) and their salts, and further, higher fatty acids and soaps, adsorb even when present in extreme dilutions (1/500,000 molar) at the mercury solution interface, pushing oxygen out of the adsorption layer (according to Michaelis and Rona's or Freundlich and Losey's displacing action, or Reichenstein's substitution principle), and thus lower the adsorption current due to reduction of oxygen; in other words, they poison the fresh electrode surface, changing the adsorption current into the diffusion one, in which oxygen has to diffuse through the adsorbed layer of surface active matter added to the solution. Electrolytes act similarly to these highly adsorbable substances, but to a much less extent. It is interesting to note that, if the adsorbable matter forms anions, the suppressive effect upon the current-voltage curve becomes most marked at the ascending part of the reduction current in the region where—according to the theory of electro-capillarity—mercury is positively charged against the solution (see fig. 10). Here the series of curves represents the reduction current of a $n/100$ solution of potassium hydroxide standing open to air, in which we notice the maximum due to the reduction of oxygen, first to hydrogen peroxide and then the second stage of the reduction (hydrogen peroxide to water), and, finally, the increase of current due to deposition of potassium. Increasing number of drops of a millimolar solution of sulpho-salicylic acid were added, and the curve each time repeatedly polarized from zero voltage. We observe the great suppressive effect upon the ascending part of the reduction current, which is very marked already with one or two drops of the millimolar acid added to 30 c.c. (*i.e.*, at a molar dilution of half a million). Of course, when added in such a dilution to an excess of alkali, the acid is present as anions of its salt, to which the suppressive action has to be ascribed. Most marked is this action with soaps, which are known to have very adsorbable anions. On the whole, divalent anions, like sulphate and carbonate, suppress more than anions of monovalent salts of equivalent concentration.

This influence of anions corresponds to what has been found previously in the suppressive action of cations which act upon maxima occurring at very negative cathodic potentials, *e.g.*, in the case of nickel (compare ⁽⁸⁾), where the suppressive action of cations considerably increases with their valency.

Fig. 10.



The removal of the discontinuous fall on the electrocapillary curves effected by addition of small quantities of surface active matter well conforms with the explanation given above, viz. that these substances are adsorbed preferentially to oxygen (compare fig. 8, where the curve *c* is the part of the electro-capillary curve when fuchsin was present in concentration 1/40,000).

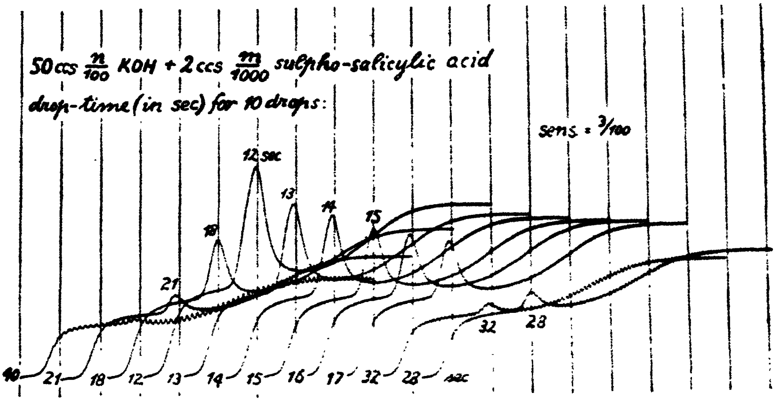
This adsorption must cause a considerable change of interfacial tension, in the same sense as the absence of oxygen, and, of course, allows the concentration-polarization to start from the very beginning of a polarizing E.M.F., just as it is in the Lippmann statical method. Thus in the presence of surface active matters in solution no Kučera' anomalies appear.

Even colloidal solutions show this effect of the removal of the discontinuous fall of electro-capillarity, as has been recently pointed out by Dr. K. Šandera [(10)], who finds that Kučera's anomalies are suppressed by the presence of colloidal matter. The same is the action of solutions containing freshly-precipitated barium sulphate, which were found to suppress the maximum at the current-voltage curve.

The Effects on Slow Drops and Stable Electrodes.

It has been pointed out that the lowering of the rate of dropping causes the discontinuous fall to appear at decreasing voltages until at infinitely slowly dropping electrodes, *i.e.*, at stable cathodes, it disappears entirely. The mentioned distinction between "old" surfaces, *i.e.*, polarizable by concentration-polarization, and "fresh" ones at which adsorption is displayed, explains also this behaviour, which is best shown in fig. 11. This shows a series of current voltage curves, all obtained from the same solution of 50 c.c. centi-normal potassium hydroxide with 2 c.c. of a millimolar sulpho-salicylic acid. Owing to the surface action of the sulpho-salicylic acid, the oxygen is almost pushed out of the interface, and in this condition adsorption in the interface is particularly sensitive to the rate of the formation of interface—*i. e.*, on dropping. Thus very fresh interfaces (quick dropping) show a still considerable amount of oxygen adsorbed (*e.g.*, curves 4, 5, 6, fig. 11), whilst somewhat older interfaces (twice slower dropping) show almost no adsorption of oxygen (*e.g.*, curves 1, 10, 11, fig. 11). Here evidently the time-effect

Fig. 11.



rigorous treatment of the subject is hardly possible with our present limited knowledge of the behaviour of neighbouring atoms in a solid, and we shall therefore only attempt to consider elasticity in an elementary way that seems adequate for the purpose in view.

The characteristic stability of a solid is almost certainly due to the powerful cohesive attraction exerted by the neighbouring atoms acting in equilibrium with an equal and opposite repulsion. Since it is known that each force is some rapidly decreasing inverse function of the distance between the atoms, how does a solid support and recover from a large stress, if its atoms are just in equilibrium under no stress, and an applied tension actually draws them apart and so reduces the cohesive bond? If the attraction and repulsion have characteristics, such as are shown in fig. 1, the tenacity and elasticity of a material can be explained. The point P corresponds to a state of no stress with the atoms under equal repulsive and attractive forces. As a tension is applied causing an external force F to come into action on the atom, the atoms separate slightly and both A and R are diminished, but R to a considerably greater extent than A. The rate of change of the *repulsion* is the main factor in determining the elasticity, the variation in the force of attraction being relatively small within the range of elastic strain. The dotted curve in fig. 1 represents the value of A—R which is equal to the applied force F. As the tension increases, a point is reached at which A—R has a maximum value: at this point the atoms will separate with further increase in tension. By our hypothesis the displacement of the atoms at this point is small compared with the field of attraction, and the maximum value of A—R is not much less than PJ, the normal cohesion under no stress. Hence the tenacity is almost entirely determined by the cohesive attraction, whereas the elastic modulus is similarly determined by the value of $\frac{dR}{dx}$, the attraction being a comparatively flexible bond.

When a compressive stress is applied, the atoms are forced nearer together and we pass upwards along both the curves. The initial rate of change of R will be the same as before, and therefore the same modulus of elasticity would be expected, which is found by experiment to be the case. Under compression no limiting value of A—R is indicated as in tension, and if there is a limit to the amount of uniform compression a solid can withstand, it cannot be realized experimentally. The hypothetical forces thus lead generally to a natural explanation of the elastic behaviour of a solid.

It can be shown more quantitatively from the known data of elasticity that the repulsion field must have a considerably higher gradient and smaller range than the attraction.

Consider any two neighbouring atoms in a body which is subjected to a uniform compression, and let the external pressure p give rise to a force F thrusting the atoms closer together. If the distance between the atoms is e, and an increment $d\mathrm{F}$ in the force produces a decrement de in this distance, we must have

$$d\mathrm{F}=d\mathrm{R}-d\mathrm{A}$$

or

$$\frac{d\mathrm{F}}{de}=\frac{d\mathrm{R}}{de}-\frac{d\mathrm{A}}{de}.$$

Now, $\frac{d\mathrm{R}}{de}$ and $\frac{d\mathrm{A}}{de}$ are both necessarily negative, and $\frac{d\mathrm{F}}{de}$ is also negative; hence $\frac{d\mathrm{R}}{de}$ must exceed $\frac{d\mathrm{A}}{de}$ for stable equilibrium to exist.

Let it be assumed that the attraction is in the neighbourhood of the point P of fig. 1 can be represented by the simple inverse relation

$$\mathrm{A}=\frac{\mathrm{B}}{e^n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

without assuming any value for the exponent n.

Then

$$\frac{d\mathrm{A}}{de}=-\frac{n\mathrm{B}}{e^{n+1}}=-\frac{n\mathrm{A}}{e}. \quad . \quad . \quad . \quad . \quad (23)$$

If K is the modulus of compressibility,

$$dp=-3\mathrm{K}\frac{de}{e};$$

and also $\mathrm{F}=\beta e^2 p$, where β is a factor not greatly different from unity and dependent on the type of atomic packing.

Hence

$$d\mathrm{F}=-3\mathrm{K}\beta e\,de$$

or

$$\frac{d\mathrm{F}}{de}=-3\mathrm{K}\beta e. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We can also write $\mathrm{A}=\beta e^2 f$, where f is a stress which corresponds to the limiting cohesion between the atoms.

This stress f represents the ideal tenacity or the tenacity under a state of triple tension.

Hence $$\frac{dA}{de} = -\frac{nA}{e} = -\beta nef.$$

So that $$\frac{dF}{de} = \frac{3K}{nf}\frac{dA}{de}$$

and $$\frac{dR}{de} = \frac{dF}{de} + \frac{dA}{de} = \left(\frac{3K}{nf} + 1\right) \times \frac{dA}{de}. \quad . \quad . \quad (25)$$

Considering the quantity within brackets, although there is much uncertainty as to the value of the ideal tenacity f, there is little doubt that this is a stress considerably smaller than the modulus K. As regards the exponent n, there is again a lack of definite knowledge, but values 2 or 4 are frequently suggested. For our present purpose we may at least regard n as not greatly different from 3, so that we can conclude from equation (26) that the elastic properties of matter qualitatively support our assumption that $\frac{dR}{de}$ considerably exceeds $\frac{dA}{de}$, even if they yield no very definite numerical information as to the ratio of the two force gradients.

That the total range of the repulsion force is small compared with the range of the attraction is also supported by another physical property of solids. It is well known that the total dilatation of a solid from absolute zero to its melting-point is approximately constant for nearly all substances, and amounts to about 0·02 in linear dimensions. Thus the complete range of the solid state corresponds to an expansion of the atomic lattice of only about 2 per cent., beyond which the solid condition of equilibrium vanishes. This quantity, in terms of our hypothesis, must be associated with the effective range of the repulsion. The attraction between atoms, on the other hand, is known to extend for a distance at least exceeding the distance between the atoms.

The author wishes to express his thanks to Sir J. E. Petavel and Mr. J. E. Sears for their continued interest and encouragement, and also to Sir T. E. Stanton and Sir W. B. Hardy for kindly reading and criticizing his first investigation into a subject which owes so much of its advance to them.

CVII. *The Size of the Molecules of Fatty Acids.* *By* F. J. HILL, *B.Sc., Research Student at the University College of the South-West of England, Exeter*[*].

1. *Introduction.*

THE effect on the surface tension of the addition of small quantities of oil to water has been widely studied. The experiments of Devaux[†], Rayleigh[‡], Marcelin[§], and Miss Pockels[‖] show that very thin oil films do not alter appreciably the surface tension, but that the tension suddenly begins to decrease when a certain critical layer of oil is placed upon the water surface. With thicker films the value approaches the surface tension of the pure oil. It is assumed that the amount of oil necessary to give the critical point at which the surface tension changes corresponds to a layer of thickness one molecule. This assumption is now generally accepted and has been confirmed by X-ray analysis. Langmuir[¶] has applied it in his work on the orientation of molecules of substances floating on water, and great advances have thus been made in the subject of molecular structure. He used a balance method to measure the excess pull exerted on a paper strip placed in the surface and separating a pure water surface from one contaminated by a known thickness of oil This subject has been continued with considerable success by Adam, who used an apparatus very similar to Langmuir's.

The present work describes experiments made to determine similar quantities with different apparatus. The method of obtaining the critical thickness differs a little from Langmuir's, but the calculation of results follows the same process.

The actual method employed to measure the surface tension was one combining du Nouy's "tensiometer" and Ferguson's sphere method. The apparatus designed consisted essentially of a long fine steel wire A about a metre long stretched between the two uprights B, C of a stand made of brass bars supported on levelling screws E, F.

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[*] Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S., F.Inst.P.

[†] Devaux, Rep. of Smithsonian Inst. 1913, p. 261.

[‡] Lord Rayleigh, Phil. Mag. [5] xlviii. p. 331 (1899).

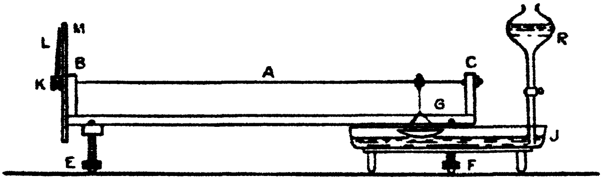
[§] A. Marcelin, *Ann. d. Phys.* [9] i. p. 19 (1914).

[‖] A. Pockels, 'Nature,' xliii. p. 437 (1891).

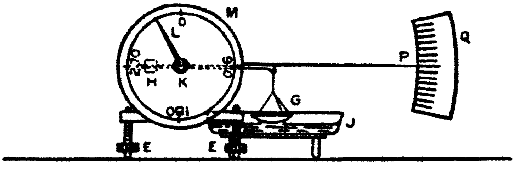
[¶] Langmuir, J. A. C. S. xxxix. p. 1848 (1917); Proc. Nat. Acad. Sci. iii. p. 251 (1917).

One end of the wire was soldered into a large screw which was fixed in the pillar C. The surface tension could then be calculated from the pull exerted on the surface of a large evaporating dish suspended from a brass arm, the latter being fixed by means of grub screws on the wire near the end C. A brass cylinder H which could be screwed along the other arm served as a counterpoise for G, and the liquid was contained in a large flat dish J. The surface of G was raised or lowered by applying a torque to the wire A by means of the brass head K fixed to the other end of the wire. The torsion was measured by the travel of the pointer L over the circular scale of degrees marked on the brass plate M.

Fig. 1.



Side View.



End View.

2. *Experiments.*

This arrangement is easy to set up, and it was found to be very sensitive, all the quantities to be measured having comparatively large values. Thus the degree of accuracy was fairly high. Although the actual values of the surface tension were not required in this work, a calibration was first made by noting the twist corresponding to a given weight placed on the evaporating dish, the latter serving as a scale-pan. In this way a linear relationship between scale reading and weight was observed. The equation used to convert scale readings into absolute force measure was that derived by Ferguson * for the raising of a sphere from a liquid surface, viz.:

$$m=4\pi\rho a^2\left\{R-\sqrt{\frac{aR}{3}}-\frac{a}{3}\right\}, \quad . \quad . \quad . \quad (1)$$

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* A. Ferguson, Phil. Mag. xxvi. p. 925 (1913).

where m is the surface tension pull, ρ the density of the liquid, $a^2\left(\equiv\frac{T}{g\rho}\right)$ the capillary constant, and R the radius of the spherical surface.

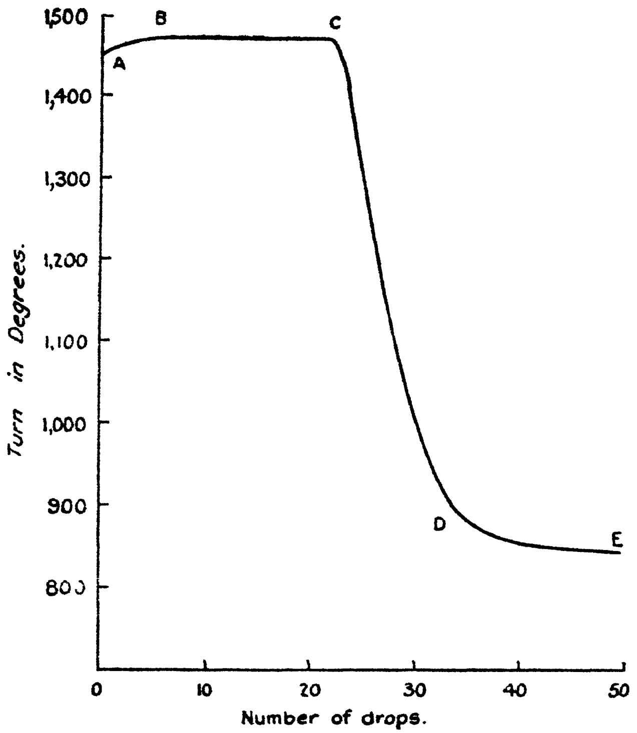
The head K was first turned so that the beam was horizontal and the pointer L exactly at the zero mark. It was arranged that the beam always returned to this zero position at every reading of the torsion made. To obtain this zero setting a long glass pointer, drawn out very fine, was attached by wax to the beam, and it moved over a reference scale Q. The actual setting was made by viewing the end of the glass pointer with a microscope set initially with the cross-wire on the image of the pointer when the latter was in the zero position.

Water was then poured into the flat dish, and to make the final adjustment the water was slowly run in from the funnel R until it just touched the surface of the dish G. The latter at this point was suddenly depressed. The pointer P was then restored to the zero position by turning the head K and the reading, given by L, noted when the image of the pointer came just on the cross-wire of the microscope. This setting could be made to within one degree, giving an accuracy of 1 in 1000.

The torque corresponding to the tension of an oily water-surface was then found. A small quantity of fatty acid—the acids actually used were oleic acid, palmitic acid, and stearic acid—was weighed and dissolved in about 100 c.c of ether. This dilute solution was allowed to fall on the water surface, the quantity being controlled by dropping the solution from a tube provided with a control tap. Five or ten drops were run out, the ether allowed to evaporate, and the twist required to bring the pointer back again to zero observed ; a few more drops were added and the process repeated. It was necessary before adding drops of solution to rotate the wire so that the beam was lowered because the addition of the ether causes a sudden lowering of surface tension as it spreads, and thus otherwise the wire would be in a state of tension greater than that necessary to suspend the dish G. The latter would then detach itself from the surface.

Using the series of readings, a graph was constructed—number of drops against number of degrees of turn. The general form of the curve is shown in fig. 2. A corresponds to pure water. Along ABC the quantity of acid on the surface is not sufficient to affect the surface tension. It appears that the slight rise A to B sometimes obtained is produced by the first portion of the ether tending to clean the surface and to drive away impurities to the edges. At C the tension decreases more or less sharply until D is reached, after which the curve becomes asymptotic to the axis of quantity of liquid at E. Thus C gives the point where there is just sufficient acid to cover the surface in an unimolecular layer. At E the value of the surface tension of the liquid in bulk is approached. The important section of the curve in this work is that around the point C, and it is advantageous to obtain as sharp a turn as possible.

Fig. 2.



Graphs were drawn for each set of readings, and the number of drops n corresponding to C determined. If the solution consists of m gm. of acid in M gm. of solution and the weight of one drop is w gm., the surface occupied by one molecule of the acid in the plane of the water surface is given by

$$\omega_M = \frac{AWM}{nwmN}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where A is the area of the water surface, W the molecular weight of the acid, and N is Avogadro's number.

The effective thickness of the molecule will then be

$$b_M = \sqrt{\omega_M}. \qquad \text{(3)}$$

The thickness of the film, *i. e.* the length of the molecule, l_M is given from

$$l_M = \frac{nwm}{MAs}, \qquad \text{(4)}$$

where s is the specific gravity of the acid.

It will be noted that the following assumptions are made:—

(i.) The value of the surface-tension changes from that of pure water when the oil film becomes unimolecular in thickness; with quantities of liquid less than this there is no alteration of the surface tension of water.

(ii.) The density of the substance in molecular form is the same as that of the substance in bulk. There is a considerable mass of evidence in support of this assumption.

3. *Experimental Results and Discussion.*

Calibration :—

Radius of spherical surface	6·762 cm.
Turn for 6 gm.	1489°
Surface tension for 1489°	74·9 dynes/cm.
Avogadro's constant	$N = 607 \times 10^{21}$
Area of water surface	$A = 604$ sq. cm.

(i.) Oleic acid, $C_{18}H_{32}O_2$.

Molecular weight	$W = 282$
Specific gravity	$s = \cdot 808$ gm./c.c.

No. of Expt.	Weight of acid, m gm.	Weight of solution, M gm.	Weight per drop, w gm.	Number of drops, n.	$\omega_M \times 10^{16}$, sq. cm.	$b_M \times 10^8$, cm.	$l_M \times 10^8$, cm.
1	·02317	71·8	·01473	10·9	54	7·4	10·7
2	·02317	71·8	·01608	10·0	54	7·4	10·6
3	·0140	73·95	·01621	18·4	50	7·1	11·6
11	·0247	34·20	·003082	21·0	61	7·8	9·4
14	·0247	34·20	·005003	14·0	55	7·4	10·3
17	·0247	34·20	·002963	24·0	55	7·4	10·5
			Mean values		54·8	7·4	10·5

(ii.) Palmitic acid, $C_{16}H_{32}O_2$.

Molecular weight .. .. $W=256$
Specific gravity .... $s=\cdot853$ gm./c.c.

No. of Expt.	Weight of acid, *m* gm.	Weight of solution, M gm.	Weight per drop, *w* gm.	Number of drops, *n*.	$\omega_M \times 10^{16}$, sq. cm.	$b_M \times 10^8$, cm.	$l_M \times 10^8$, cm.
3......	·0158	71·82	·01668	24·6	28	5·2	17·1
5......	·0158	71·82	·01649	20·5	35	5·9	15·3
7......	·0158	71·82	·01536	21·8	35	5·9	15·2
12......	·0132	32·173	·003055	44·7	36	6·0	13·9
15......	·0132	32·173	·004656	30·4	44	6·6	11·3
18......	·0132	32·173	·003035	48·0	43	6·5	11·6
			Mean values		36·8	6·0	14·1

(iii.) Stearic acid, $C_{18}H_{36}O_2$:

Molecular weight .... $W=284$
Specific gravity .... $s=1\cdot00$ gm./c.c.

No. of Expt.	Weight of acid, *m* gm.	Weight of solution, M gm.	Weight per drop, *w* gm.	Number of drops, *n*	$\omega_M \times 10^{16}$, sq. cm.	$b_M \times 10^8$, cm.	$l_M \times 10^8$, cm.
4......	·0161	73·116	·016537	24·2	32	5·6	14·6
6......	·0161	73·116	·016223	24·6	32	5·6	14·6
9......	·0080	73·966	·015448	50·2	34	5·8	13·9
13......	·0147	36·937	·0031176	77·8	29	5·4	16·0
16......	·0147	36·937	·004894	52·9	27	5·2	17·1
19......	·0147	36·937	·003144	80·3	29	5·4	16·6
			Mean values		30·5	5·5	15·5

The mean results obtained by this method are as follows:—

Oleic acid	54·8	7·4	10·5
Palmitic acid	36·8	6·0	14·1
Stearic acid	30·5	5·5	15·5

whereas Langmuir by his method finds the following :—

Oleic acid	46	6·8	11·2
Palmitic acid	21	4·6	24
Stearic acid	22	4·7	25

It may be seen that, although the results agree fairly well with Langmuir's in some cases, there are discrepancies between the values for palmitic acid and stearic acid. Thus in the present work the ratio length/breadth is respectively 1·4, 2·3, and 2·8, but he obtains 1·6, 5·2, and 5·3 respectively. Among the six results for each acid the values for oleic acid and stearic acid are quite consistent, but rather wide variations occur in the case of palmitic acid.

The sensitivity of the experiment depends upon the degree of accuracy with which the turning-point of the curve may be evaluated. It is advisable to construct a graph with a run of drops, say with the addition of five for each reading, and then repeat the experiment, concentrating on readings a little greater and less than those at the turning-point, proceeding by adding one drop only each time. The other quantities are either known accurately by independent methods (as, for example, the molecular weight or the specific gravity), or may be determined with some degree of accuracy, *e.g.*, the twist of the wire.

The degree of definition of the critical turning-point may be increased by arranging that a larger number of drops shall be used, that is, very dilute solutions may be employed. The apparatus employed possesses distinct advantages. Readings may be easily and quickly taken. The torsional motion is gradual and steady, and settings may be made to an accuracy of 1 in 1000. Experiments involving placing weights in a scale-pan to measure the pull lead to a jerky action, with consequent oscillation of the pulling surface. For simplicity of action the torsion method surpasses the balance method. The same apparatus may be modified for use with an expanding or contracting film such as Langmuir used, instead of the boundaries being fixed and more acid being introduced as described in the present work.

The writer is gratefully indebted to Dr. F. H. Newman for his helpful suggestion and criticism in this work.

CVIII. *Note on a Geometrical Radiation Theorem.*

By C. E. Wright *.

1. RECENT papers in this Journal dealing with the question of the illumination of a surface by radiation transmitted through an aperture suggest that the following treatment of some particular cases may be of interest.

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* Communicated by the Author.

Some reductions of the general integral to cases of double integration only are discussed in most text books on geometrical optics ; for the cases to be considered in this note more special methods will suffice, and are perhaps easier of application.

2. An area situated in a plane transmits uniform intensity I per unit area. The illumination of a second area in a parallel plane, the distance between the planes being l, is to be considered. A straight line perpendicular to the planes meets them in points O, O_1, origins of parallel sets of rectangular axes (Ox, Oy), (O_1x', O_1y'). The general expression for intensity becomes

$$\mathrm{I}l^2\int\int\int\int\frac{dx\,dy\,dx'\,dy'}{\{(x-x')^2+(y-y')^2+l^2\}^2}. \quad . \quad . \quad (1)$$

The case to be considered deals with similarly oriented rectangles (with sides parallel to the axes) in the two planes. The limits for the integrations are then constants, and from this the following simplification is derived. Since x and $-x'$ are similarly involved, let $x-x'=u$. For the integration with respect to x, $du=dx$; on substitution of constant limits (as x_1) the substitution $x_1-x'=u$, $-dx'=du$ reduces the integration $\int\int dx\,dx'$ to $-\int\int(du)^2$. Similarly for y and y'.

Write $x-x'=u$, $y-y'=v$, expression (1) becomes

$$\mathrm{I}l^2\int\int\int\int\frac{(du)^2\,(dv)^2}{(u^2+v^2+l^2)^2}.$$

Degenerate cases occur involving fewer integrations. Hence it is desirable to obtain the results of the successive integrations, which are as follow :—

$$\mathrm{I}l^2\int\int\int\int\frac{(du)^2(dv)^2}{(u^2+v^2+l^2)^2}$$

$$=\tfrac{1}{2}\mathrm{I}l^2\int\int\int\frac{du(dv)^2}{(v^2+l^2)^2}\left\{\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}}+\frac{u(v^2+l^2)^{\frac{1}{2}}}{u^2+v^2+l^2}\right\}. \quad (a)$$

$$=\tfrac{1}{2}\mathrm{I}l^2\int\int\frac{(dv)^2}{(v^2+l^2)^{\frac{3}{2}}}u\,.\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$=\tfrac{1}{2}\mathrm{I}\int dv\left\{\frac{uv}{(v^2+l^2)^{\frac{1}{2}}}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}}+l\tan^{-1}\frac{l}{v}\right.$$

$$\left.-(l^2+u^2)^{\frac{1}{2}}\tan^{-1}\frac{(l^2+u^2)^{\frac{1}{2}}}{v}\right\} \quad . \quad . \quad . \quad . \quad (c)$$

$$=\tfrac{1}{2}\mathrm{I}\Big[u(v^2+l^2)^{\frac12}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac12}}-\tfrac{1}{2}l^2\log(u^2+v^2+l^2)$$

$$+lv\tan^{-1}\frac{l}{v}+\tfrac{1}{2}l^2\log(v^2+l^2)-(l^2+u^2)^{\frac12}v\tan^{-1}\frac{(l^2+u^2)^{\frac12}}{v}\Big], \quad .\ .\ .\ (d)$$

and to complete the necessary list,

$$\mathrm{I}l^2\iint\frac{du\,dv}{(u^2+v^2+l^2)^2}$$

$$=\tfrac{1}{2}\mathrm{I}\Big[\frac{v}{(v^2+l^2)^{\frac12}}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac12}}-\frac{u}{(u^2+l^2)^{\frac12}}\tan^{-1}\frac{v}{(u^2+l^2)^{\frac12}}\Big]. \quad .\ .\ .\ (e)$$

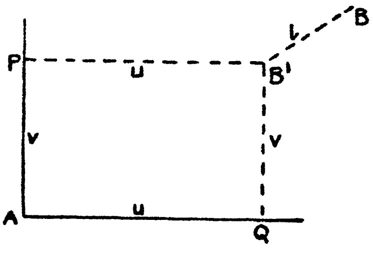
3. Since the limits are constants, functions of v (or u) only may be omitted in (d); it is also convenient to write

$$\tan^{-1}\frac{(l^2+u^2)^{\frac12}}{v}=\tfrac{1}{2}\pi-\tan^{-1}\frac{v}{(u^2+l^2)^{\frac12}},$$

and the integral then reduces to the form

$$\tfrac{1}{2}\mathrm{I}\Big[u(v^2+l^2)^{\frac12}\tan^{-1}\frac{v}{(v^2+l^2)^{\frac12}}+v(u^2+l^2)^{\frac12}\tan^{-1}\frac{v}{(u^2+l^2)^{\frac12}}$$

$$-\tfrac{1}{2}\pi v(l^2+u^2)^{\frac12}-\tfrac{1}{2}l^2\log(u^2+v^2+l^2)\Big]. \quad (f)$$



Let A be any corner of one rectangle, B any corner of the second, B′ the projection of B on the plane of the first, B′P, B′Q, AP, AQ parallels to the axes as shown. The integral is

$$\sum\sum_{\mathrm{AB}}\pm\,.\{\mathrm{B'Q}\,.\,\mathrm{BP}\,.\,\angle\mathrm{ABP}+\mathrm{B'P}\,.\,\mathrm{BQ}\,.\,\angle\mathrm{ABQ}$$

$$-\tfrac{1}{2}\pi\mathrm{B'P}\,.\,\mathrm{BQ}-l^2\log\mathrm{AB}\},$$

with proper assignation of the signs.

Even with this reduction, the insertion of general limits leads to complicated expressions. The physical interpretation gives, however, a curious analytical result when the planes of the two rectangles coincide ; for

$$\operatorname*{Limit}_{l\to 0} \mathrm{I}l^2\iint\frac{(du)^2(dv)^2}{(u^2+v^2+l^2)^2}=\pi\mathrm{I}$$

$$\times \text{area common to the two rectangles.}$$

The similar theorem is deduced for two concentric circles (Prof. E. A. Milne, Phil. Mag. [7] vii. p. 275, Feb. 1929), and is readily deduced for concentric squares from results set out below. Hence for rectangles

$$x=a \text{ to } b,\quad y=c \text{ to } d,\quad x'=e \text{ to } f,\quad y'=g \text{ to } h,$$

the value of

$$\operatorname*{Limit}_{l\to 0}\int_a^b dx\int_c^d dy\int_e^f dx'\int_g^h dy'\{x-x')^2+(y-y')^2+l^2\}^{-2}$$

$$(a<b,\quad c<d,\quad e<f,\quad g<h),$$

considered as a function of e, f, g, h, $=\pi\mathrm{I}(b-a)(d-c)$ if $e<a<b<f$, $g<c<d<h$ is zero if $(a,b)\lessgtr(e,f)$, $(c,d)\lessgtr(g,h)$, whilst if e or f lies between a and b, and g or h lies between c and d, the integral is linear in the variable or variables which occur in the statements of inequality.

These results cannot readily be obtained from the form of the integrand ; in fact effective elements of the integral arise, in the limit, for zero values of both u and v, whence expansion of the integrand in ascending powers of l is impossible.

4. The results for coaxial squares (with parallel sides of lengths $(2a, 2b)$) admit of reduction. In the form § 3 (f), the first two terms now contribute equal amounts, the third term gives zero. The final result may be written

$$\mathrm{V}=4\mathrm{I}\left\{p(p^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{p}{(p^2+l^2)^{\frac{1}{2}}}-p(q^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{p}{(q^2+l^2)^{\frac{1}{2}}}\right.$$
$$+q(q^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{q}{(q^2+l^2)^{\frac{1}{2}}}-q(p^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{q}{(p^2+l^2)^{\frac{1}{2}}}$$
$$\left.-\tfrac{1}{4}l^2\log\frac{(2p^2+l^2)(2q^2+l^2)}{(p^2+q^2+l^2)^2}\right\},$$

with $p=a+b$, $q=a-b$.

For equal squares, $p=2a$, $q=0$ gives

$$4\mathrm{I}\left[2a(4a^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{2a}{(4a^2+l^2)^{\frac{1}{2}}}-2al\tan^{-1}\frac{2a}{l}\right.$$
$$\left.-\tfrac{1}{4}l^2\log\frac{l^2(8a^2+l^2)}{(4a^2+l^2)^2}\right];$$

If in this $l=2a\xi$, $\mathrm{V}/16a^2\mathrm{I}=\eta$, the relation between ξ and η is given by

$$\eta=(1+\xi^2)^{\frac{1}{2}}\tan^{-1}\frac{1}{(1+\xi^2)^{\frac{1}{2}}}-\xi\tan^{-1}\frac{1}{\xi}-\tfrac{1}{4}\xi^2\log\left\{1-\frac{1}{(\xi^2+1)^2}\right\}.$$

From this, or from the previous form, the known limiting cases when $l\rightarrow 0$ or $l\rightarrow\infty$ may be obtained. Between $\xi=0$ and $\xi=\infty$, η continually decreases.

The special case treated by Dr. L. F. Richardson (Phil. Mag. [7] vi. p. 1019, Nov. 1928) requires $\xi=1$, giving

$$\mathrm{V}=\mathrm{I}l^2\left[4\sqrt{2}\tan^{-1}\frac{1}{\sqrt{2}}-\pi+\log\frac{4}{3}\right]=0\cdot6278\mathrm{I}l^2.$$

5. Let the results (*a*), (*b*), (*c*) of § 2 be written

$$\iiint du(dv)^2\,.\,\phi_1,\qquad \iint(dv)^2\,.\,\phi_2,\qquad \int dv\,.\,\phi_3\qquad\text{respectively,}$$

and let $u=x-x'$, $v=y-y'$, unless otherwise stated. The following cases are now deducible.

In ϕ_1 write $y=c$, and take the result between limits $x=-a$ to $+a$. On multiplication by α, the result gives the intensity of illumination at (x', y') due to a slit of breadth α extending from $x=-a$ to $+a$ along the line $y=c$.

Multiply $-\phi_2$ by $\alpha\beta$, write $y=c$, $y'=c'$, and take the result between limits $x=-a$ to $+a$, $x'=f$ to g. The result is the illumination on a slit situated on $y'=c$, of breadth β and extending from $x'=f$ to $x'=g$, due to an illuminating slit of breadth α and length $2a$ placed along the line $y=c$.

ϕ_3 with change of sign similarly gives the illumination, due to a rectangle in one plane, of a slit in the other plane parallel to one edge of the rectangle.

Finally, (*e*) may be interpreted so as to give the illumination on a straight slit due to a perpendicular slit in the parallel plane *.

6. The above method admits of application to other problems of a physical nature. Some of these applications will, it is hoped, be dealt with in a future note.

Blackheath.
March 11, 1929.

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* The intensity of illumination at any point in space due to illumination by a rectangle can also be derived from (*e*).

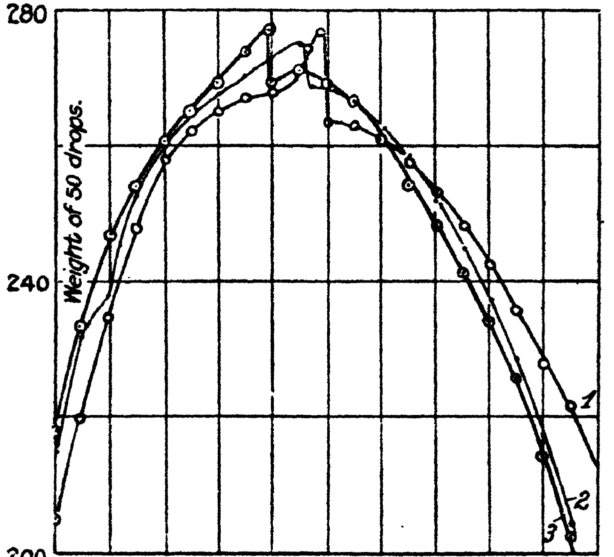
CIX. *Electrolysis with a Mercury Cathode.*—Part II. *Explanation of the Anomalies on the Electro-capillary Curves.*

By Jaroslav Heyrovský, *D.Sc., Ph.D., Professor in Physical Chemistry, and* Rudolph Šimůnek, *Ph.D., Assistant in Experimental Physics, Charles' University, Prague* *.

Introduction.

As mentioned in Part I. of the above communication (1), we owe to Prof. B. Kučera the introduction of the drop-weight method for the determination of the interfacial tension of polarized mercury. However, the electro-capillary curves thus obtained often differ considerably from those obtained by Lippmann's classical method by means of the capillary electrometer. In some solutions Kučera's curves deviate from the ordinary electro-capillary parabolas by exhibiting a marked anomalous maximum of interfacial tension (see fig. 1), which at a certain polarizing E.M.F.

Fig. 1.



(1) $n/1000\ H_2SO_4$. (2) $n/500\ Na_2SO_4$.
(3) $n/100\ K_2SO_4$.

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* Communicated by the Authors.

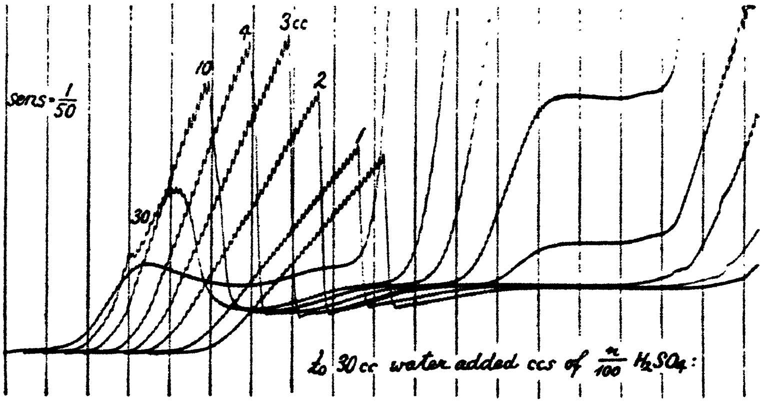
abruptly falls to coincide again with the regular course of the parabola.

Professor B. Kučera himself described the occurrence of these anomalies in two of his communications (2) (3), and suggested to the present authors to investigate the cause of these anomalies from the physico-chemical standpoint. A preliminary report of these investigations has been published in the *Bulletin International de l'Académie des Sciences de Bohême*, 1927, presented October 21st. In the following these anomalous maxima of interfacial tension will be called Kučera's anomalies.

Experimental.

The measurements were first carried out as described by Prof. Kučera by keeping the electrolyte solution in a beaker open to the air. A layer of mercury at the bottom of this beaker served as anode and the mercury drops falling slowly from a thick-walled glass capillary as cathode. The polarization was effected by connecting these electrodes to the terminals of a resistance-box potentiometer adjusted so that 1 millivolt of the E.M.F. corresponded to 1 ohm in the box (compare Part I. p. 305, fig. 2). The source of the E.M.F. was a 2- or 4-volt accumulator. Aqueous solutions of sulphuric acid and sodium and potassium sulphate in various dilutions were used as electrolytes, some 60 solutions having been thus investigated.

Fig. 2.



To find the region of concentrations in which Kučera's anomalies are most prominent, the concentrations were consists of the more adsorbable matter gradually pushing out the less adsorbable one—*i. e.*, oxygen. In such a case stable electrodes could not show any adsorbed oxygen, and therefore exhibit no adsorption current but merely a diffusion one being at the same time perfectly polarizable.

Polarographic curves obtained when polarizing a small steady mercury surface exposed to air and using a milli normal electrolyte without any surface active matter, do not show any reproducible maxima, which would be independent of the duration of polarization unless the solution be agitated. When vigorously stirring the solution the same maxima occur on current-voltage curves the position of which is independent of the duration of polarization, and to a small extent it depends on the direction in which we change the polarizing E.M.F. (*i. e.*, the hysteresis effect already mentioned). Here, no doubt, the mercury-electrode surface is kept a "fresh" one by stirring—like the dropping cathode—*i. e.*, it is an electrode at which the concentration-polarization is prevented, and thus the adsorption current manifests itself; when, however, the stirring ceases the concentration-polarization soon starts, the surface being transformed into an "old" one, which is indicated by the sudden fall of the current, exactly similar to the fall which accompanies Kučera's anomaly.

The authors gratefully acknowledge grants of the Czech Academy of Science, which enabled them to carry out these polarographic investigations.

Summary.

1. Current-voltage curves obtained in electrolysis with the dropping mercury cathode when solutions standing open to the air are polarized, show prominent well-reproducible maxima due to the direct electro-reduction of dissolved atmospheric oxygen. The maxima are most prominent and discontinuous in ca. millinormal solution of electrolytes.

2. The fall of the current at the maximum is accompanied by a sudden fall of the interfacial tension at the polarized mercury-dropping cathode and a sudden increase of the cathodic potential.

3. The maxima of the current as well as those of the interfacial tension are suppressed by surface-active matter, active anions, or great concentrations of electrolytes. These phenomena are explained by preferential adsorption.

4. The discontinuous changes of electro-capillarity, which were first described by Prof. Kučera, *i. e.*, "Kučera's

anomalies," as well as the maxima of the current are explained by the setting in of the concentration-polarization, which prevents further adsorption of oxygen at the mercury-solution interface. Similar current maxima are well observable on small stable mercury cathodes when the solutions are stirred.

References.

(1) Jar. Heyrovský, Phil. Mag. xlv. p. 303 (1923).
(2) B. Kučera, *Annalen der Ph.* iv. 11, pp. 529, 693 (1903).
(3) B. Kučera, *Bulletin international de l'Académie des Sciences de Bohême*, 1903.
(4) J. Rasch, Dissertation, Charles University, 1928.
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CX. *On the Ionization of Hydrogen by its own Radiations.* *By* JOHN THOMSON, *M.A.*, *B.Sc.*, *Carnegie Research Fellow in the University of Glasgow*[*].

Introductory.

IN a recent paper[†] the writer described a preliminary investigation of the ultra-violet ionizing radiations emitted by point discharges in various gases. Experiments performed in hydrogen appeared to indicate that this gas was ionized by its own radiations, and attention was called to this rather remarkable phenomenon in the discussion of the results. The experiments then described, however, were not primarily intended to investigate this effect, and did not appear (to the writer and others) to be absolutely conclusive. There was a possibility that the ionization observed was due to traces of water-vapour in the gas or on the electrodes.

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[*] Communicated by Prof. E. Taylor Jones, D.Sc.

[†] Phil. Mag. vi. p. 526 (1928).

The present communication describes an investigation the sole object of which was to determine if pure dry hydrogen gas is ionized by radiations emitted by a point discharge in the same gas. The results obtained appear to justify the assumptions previously made, showing that the presence of impurities in the gas or on the electrode surfaces is not a necessary condition for ionization to occur. In a note at the end of the paper the experiments of Chattock and Tyndall on the electrical wind in hydrogen are discussed with reference to the present investigation.

Experimental Methods.

It may be well to indicate briefly the theory of the experiments described in the previous communications. The radiations investigated are of such a nature that the only solid substance through which they are transmitted with sufficient intensity to be detected is a celluloid film. Consequently the radiations were produced and detected in the same tube. The point discharge took place in the region P of the discharge-tube. The radiations emitted were detected by their ionization and photo-electric effects in the region Q. Between P and Q an arrangement of shields was placed to ensure that no ions could travel from the discharge to the ionization chamber. Examples of such tubes for producing and detecting the radiations are given in figs. 1 and 2 of the present paper and in fig. 1 of the previous communication.

The first series of experiments was made, using discharge tubes which had not been "baked out." The aim of these experiments was to trace any changes which might occur in the ionization current at Q due to the radiations emitted at P, as the gas, walls, and electrodes became gradually free from water-vapour and gases other than hydrogen. In order to obtain the necessary insulation in such a tube, filled with moist gas, it was necessary to use a wax sealing round the electrode which measured the ionization current. Consequently such a tube could not be "baked out" at any stage of the investigation.

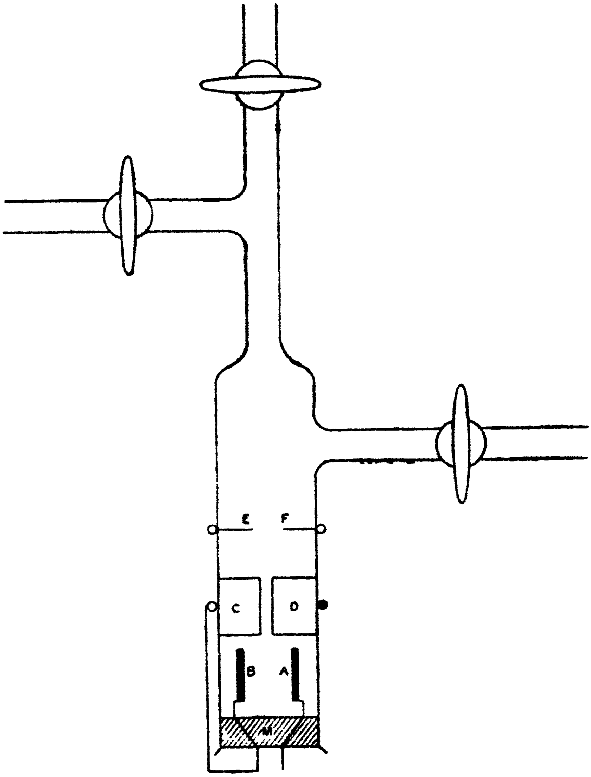
The second series of experiments was therefore performed with a different set of tubes. These tubes were "all glass and metal-seal-in," so that they might be "baked out" at a high temperature. By this means the attempt was made to measure the ionization current at Q when the tube and electrodes had been thoroughly dried and "outgassed," the hydrogen which was admitted being pure and dry.

Lastly, it must be mentioned that all these experiments were performed at approximately atmospheric pressure, thus removing many of the dangers of impurities which arise when the pressure is low.

Unbaked Tubes and Electrodes.—The first set of experiments was made with the discharge-tube represented diagrammatically in fig. 1.

A glass cylinder 2 cm. in diameter was connected to three side-tubes. These led to the pump, the mercury pressure-gauge, and the gas system. E and F were the points of two platinum electrodes, half a centimetre apart, and between them the discharge passed. Throughout all the experiments the discharge current was maintained at 1 milliamp. C and D were two brass half-cylinders arranged to prevent the passage of ions from the discharge to the ionization chamber. The slot between them was 2 mm. wide and the cylinders were 2 cm. long. The ionization chamber contained the two rectangular electrodes A and B, the former

Fig. 1.



being connected to the electrometer. These electrodes were so arranged that no radiation from EF fell *directly* upon them. That they would collect scattered radiation cannot be doubted.

The tube was sealed at M with a mixture of beeswax and resin. While experiments were being performed, C and B were at a potential of −380 volts with respect to A, which was initially at earth potential. The potential of D was +300 volts relative to the earth. The lead from A to the electrometer was carefully shielded.

The gas was obtained by the electrolysis of barium hydroxide in a specially constructed Hoffmann's apparatus. The anode was placed half-way up one of the arms at a distance of 30 cm. from the bottom. There was therefore no possibility of any diffusion of oxygen into the hydrogen arm. The gas then passed through a liquid-air trap and a capillary tube to the discharge apparatus. The pump used was a Cenco Hyvac, since very low pressures were not required.

As already stated, the method of investigation adopted was to attempt to dry the gas and discharge-tube progressively by means of liquid air. Starting with moist gas, readings were taken of the ionization current at A when the discharge was passing at EF. Then liquid air was placed round the trap, and the dry gas was passed into the tube. Here it no doubt received water-vapour from the walls and electrodes and became relatively moist again. A reading of the ionization current was again taken. This process of admitting dry gas and of measuring the ionization current was continued for some considerable time until the ionization current became constant.

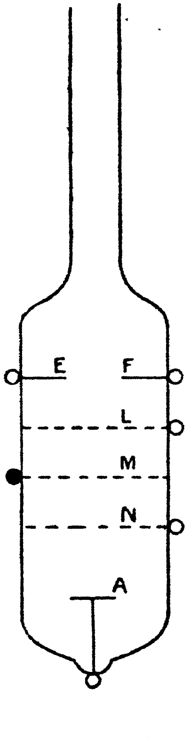
The results of this experiment are shown in the table below. The column "No. of experiment" indicates the order in which the experiments were taken: 1 and 2 refer to moist gas; during 3 to 10 the gas was being progressively dried by the method indicated above.

No. of experiment...	1	2	3	4	5	6	7	8	9	10
Ionization current...	3	3	4	8	21	30	42	56	56	56

After the ionization current had become constant, a series of readings was taken of the current at different pressures. These readings gave a curve in remarkable agreement with that obtained using moist gas, and obtained under the same conditions (curve (*a*) in fig. 2 of the previous paper).

Similar experiments were attempted with different discharge-tubes designed to prevent *any* radiation from EF impinging upon A or B. The elaborate precautions which were necessary, however, caused A and B to be removed too far from the discharge, and narrowed the beam of radiation greatly. The results with such tubes were never satisfactory on account of this weakening in the intensity of the radiation between A and B. Disturbing effects which were ultimately traced to charge on the walls and the relatively large distance between A and B became prominent. This type of experiment had to be abandoned.

Fig. 2



Baked-out Tubes and Electrodes.—The second experiment required a tube of the "all glass and metal-seal-in" type. This is represented in fig. 2. Every precaution was taken to ensure that no impurities of any description would interfere with the investigation. The gas system was similar to that used previously, except that another liquid-air trap was inserted between the capillary tube and the discharge-tube. No mercury gauge was used, and a single two-way vacuum stop-cock connected the pump, gas system, and discharge-tube. All the connexions were glass-sealed.

In the tube itself, L, M, N were disks of wire gauze, and A was a small copper plate. These were heated strongly before they were sealed into the tube, to remove as much occluded gas and vapour as possible. Then the tube was placed in a small electric furnace and baked out at about 350° C. for about 4 hours at a high vacuum. As the tube cooled it was immersed in a paraffin-wax bath in order to coat the outer surface of the glass with a good insulator. Pure dry hydrogen was then admitted to approximately atmospheric pressure.

As in the previous work, the discharge current of 1 milliamp. passed between the points of the platinum electrodes E and F. The gauze L, which was at a distance of 1 cm. from EF, was maintained at a potential of +300 volts relative to the gauze M. The latter was 1 cm. from L and at earth potential. The gauze N, 1 cm. below M, was maintained at −370 volts, while the plate A, connected to the quadrant electrometer and initially at earth potential, was 1·4 cm. from N. This arrangement of potentials and distances effectively screened the plate A from any currents due to ions produced above the gauze N. It also prevented the passage of photo-electrons from N to A, since the field between N and M was greater than that between N and A.

Experiments with this apparatus showed that when the discharge was passed across the gap EF, the plate A became charged negatively. This current ceased immediately after the discharge was cut off. It appeared to be a true ionization current due to the gas between N and A. The current remained very constant when the discharge current remained constant. It appeared to be quite independent of the number of times that the discharge had already been passed. Moreover, as in a former experiment described in the previous paper, the ionization current increased linearly with the discharge current, as the latter was varied between 0·4 and 1·6 milliamp.

Analysis of the Results.

It appears to the writer that the first series of experiments admits of only one interpretation. The only effect of placing the liquid air round the trap was to dry and purify the gas. As the gas, tube, and electrodes became drier, the ionization increased. The ionization, therefore, must be due to the gas itself. The explanation of the increase in the current may be interesting, but as far as the present experiments are concerned, it is a matter for conjecture. That the result is not quite anomalous is shown by the peculiar results obtained by Chattock and Tyndall * on the electrical wind in very pure hydrogen. These writers have shown that when the gas is very pure, there is a large apparent increase in the velocity of the negative ions emitted by the point in a point-to-plane discharge. That their results are closely connected with those of the present investigation is shown at the end of this communication.

The second experiment is even more conclusive. The currents measured were very large indeed, and remained constant over a large number of experiments. This suggests that no changes were taking place in the gas-content of the tube, an effect which had caused considerable difficulty during earlier observations.

Theoretical Considerations.—The result of the investigation appears to the writer to be of some theoretical importance. In the paper already mentioned † attention was directed to the fact that F. L. Mohler ‡ was unable to detect any photo-ionization of hydrogen by its own radiations. His experiments were performed at a pressure of about 0·02 mm., however, and his result is not necessarily contradictory to that of the present investigation. The conclusion which he draws from his experiment is that, not only are H_2 and H unable to emit radiation capable of directly ionizing H_2, but that H_2^+ has also an ionizing potential which is less than 15·9 volts.

From the present experiments no conclusion of this nature regarding ionization potentials can be drawn. If it could be assumed that the gas in the ionization chamber was normal hydrogen and that the ionization took place in one stage, then the result would contradict Mohler's conclusion; but neither assumption is justifiable. The high pressure in the ionization chamber favours interchanges of energy between excited molecules; and it appears to the writer that this is the most probable explanation of the observed ionization. Having regard to Mohler's conclusion, it may be asserted that the ionization is brought about by two-stage excitation, due to molecules absorbing two or more quanta of energy, either from the radiations or by collisions with excited molecules.

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* Phil. Mag. xix. p. 449 (1910).

† Thomson, *loc. cit.*

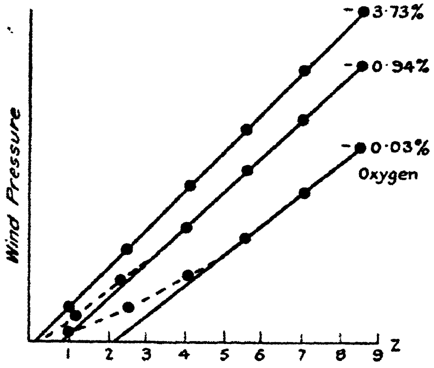
‡ Proc. Nat. Acad. Sci. xii. p. 494 (1926).

Note on the Investigation by Chattock and Tyndall of the Pressure of the Electrical Wind.

The writer's attention was called to this investigation by Professor Tyndall at the Glasgow meeting of the British Association. The primary object of the experiments was to determine the velocity (V) of gas ions in a field of 1 volt/cm. "Earlier measurements by the wind-pressure method* led to values of V which are in satisfactory agreement with those obtained by other methods," but in the particular case of hydrogen the velocity of the negative ions varied very considerably with the purity of the gas.

It may be well to sketch briefly the theory of the experiment. A controlled current of a few microamperes flowed from a sharp platinum point A to a circular perforated plate B, the point and plate being enclosed in an air-tight tube. By means of the sensitive manometer invented by one of the authors for this purpose, it was possible to measure the pressure of the electrical wind at the plate B. A could be moved so that the distance AB (z) could be varied. The experiment consisted in measuring the pressure of the wind p for different values of z, and by this means obtaining $\frac{dp}{dz}$. This allowed the specific velocity of the ions to be calculated.

Fig. 3.



The curves shown in fig. 3 (curves II. in the communication of Chattock and Tyndall) were obtained by plotting

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* Phil. Mag. i. p. 79 (1901).

p against z, each curve corresponding to a different percentage of oxygen impurity in the gas. In each case, when z is large $\frac{dp}{dz}$ is constant, and this is the result predicted by the authors' theory. It will be noted, however, that as the hydrogen becomes purer, $\frac{dp}{dz}$ decreases, while z_0, the intercept on the z-axis made by the straight part of the curve produced, increases. Chattock and Tyndall explain the decrease in $\frac{dp}{dz}$ as the gas becomes purer by the hypothesis that there is back-discharge from the plate to the point, and this discharge increases as the percentage of oxygen impurity decreases. How the back-discharge is produced they do not suggest.

Two possible explanations are given by the authors of the increase in z_0 which accompanies the decrease in oxygen impurity, viz.:—

(i.) "The ions from the point may travel an appreciable distance before growing large enough to produce much wind."

(ii.) "The gas may be ionized for an appreciable distance from the point—this being equivalent to a lengthening of the point as far as wind-production is concerned."

Both of these phenomena are supposed to be enhanced as the gas becomes purer.

The purpose of the present note is to suggest an explanation of the manner in which the back-discharge in these experiments arises, and of the reason why it increases as the gas becomes purer. The same explanation accounts for the existence of z_0, and for its increase as the oxygen impurity diminishes.

It has been shown by Wynn-Williams * and the present writer † that a metallic point such as that used by Chattock and Tyndall gives rise to electromagnetic ionizing radiations. These have been shown to emanate, not from the point itself, but from the gas in its immediate vicinity, and in the case of an air discharge from gas within 2 to 3 mm. from

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* Phil. Mag. i. p. 353 (1926).

† *Loc. cit.* v. p. 513 (1928).

the point. In air such radiations can produce ionization up to a distance of about 3 cm. from their source; beyond his they cannot be detected. It has also been shown that the intensity of the radiations is a linear function of the current flowing in the discharge.

This, then, appears to afford the explanation of the back-discharge postulated by Chattock and Tyndall. Considering first the case of impure hydrogen, z_0 is of the order of 4 mm. and the back-discharge is small. Even in this case, however, the writers found that $\frac{dp}{dz}$ increased as the current in the discharge decreased. This certainly indicates the existence of back-discharge. Moreover, it may be correlated with the fact mentioned above that the intensity of the ionizing radiations increases linearly with the discharge current.

The authors explain the normal z_0 (4 mm.) by means of Franck's hypothesis that the ions do not reach their full size while travelling a distance comparable with 4 mm. They find it difficult, however, to explain by this supposition the increase in z_0 as the gas becomes purer. A satisfactory explanation may be given in terms of the ionizing radiations. In order that radiation may occur, recombination or at least inelastic impact of ions with molecules must take place. Hence, within a distance of 3 mm. from the point, many of the ions will lose their charge or their velocity. But the radiations emitted in this region would cause ionization, and in a short distance the excess of negative ions would be re-established. This would account for the existence of z_0, and an examination of the results given in the previous paper by the present writer will show that the theory can be applied to both positive and negative discharges in air or in hydrogen.

The most interesting phenomenon, however, from the point of view of the present paper is the decrease in $\frac{dp}{dz}$ and the increase in z_0 as the hydrogen becomes purer. It has been shown earlier in the present communication that the ionization in hydrogen, due to radiations emitted by a point discharge in the same gas, increases enormously as the gas is purified. In the experiments described the impurity was water-vapour, but it must be remembered that the passage of the discharge would decompose part of the water and cause oxygen impurity. It is indeed remarkable that this result should agree so well with the experiments of

Chattock and Tyndall. The increase in back-discharge as the gas became purer, the increase in z_0 from 4 mm. to 3 cm., are exactly what would be expected if the radiations became more intense and the gas itself a more perfect absorber. There appears to be no doubt that radiation is more easily excited in the pure gas, since the authors observed that "in the purest hydrogen and for a negative point the whole plate glows brightly over the surface presented to the point." At the end of their communication they remark: "The four phenomena of glow, fall of wind-pressure, shift of negative curve (increase of z_0), and abnormally rapid combination, all take place within about the same narrow limits of oxygen percentage; it is therefore at least tempting to think that they may all ultimately prove traceable to a single source." It appears to the writer that this source is to be found in the variations in the intensity of the radiations emitted by the gas in the vicinity of the point during the discharge.

Summary.

1. Experiments are described showing that hydrogen is ionized by radiations emitted by a point discharge in the same gas. It is suggested that the ionization takes place in stages, the molecules absorbing two or more quanta of energy, either from the radiations or by collisions with other excited molecules.

2. The results of this and preceding investigations by the same writer are applied to the investigation by Chattock and Tyndall of the pressure of the electrical wind. It is shown that several peculiar phenomena encountered by these experimenters can be satisfactorily explained by a consideration of the ionizing radiations emitted by the gas in the immediate neighbourhood of metallic points charged to a high potential.

In conclusion, the writer again wishes to express his indebtedness to Professor Taylor Jones for his advice and encouragement. He also wishes to thank the Carnegie Trust for a much-appreciated grant for apparatus.

February 1929.

CXI. *The Effect of Stress upon the X-Ray Reflexions from Tungsten Wire at Air Temperature.* *By* H. L. Cox, *B.A.*, *and* I. Backhurst, *M.Sc.* (*both of the National Physical Laboratory*)*.

[Plate XXII.]

Introduction.

In connexion with fundamental research on the deformation of metallic single crystals, it appeared to be of interest to determine whether the application of stress to a single crystal was capable of producing elastic deformation of the space lattice either in part or in whole. Should the lattice as a whole be distorted, evidence of the distortion could be obtained by recording the relative movements of the crystallographic planes as determined by X-ray examination. Should only portions of the lattice be affected, *e. g.*, by deformation in the neighbourhood of cracks, the distortion would be evidenced by a blurring of the spots obtained by reflexion of X-rays from the crystallographic planes. In either case the crucial point would be whether, upon removal of the stress, the X-ray diagram obtained returned to its original appearance before the stress was applied.

With this object in view, it was decided to take X-ray photographs of a single crystal, firstly unstrained, and then under a series of stresses of gradually increasing magnitude. It was intended to watch each successive photograph for any change in appearance, and, as soon as any alteration was remarked, to take a final photograph in the unstrained state in order to determine whether the change was permanent.

Description of Experiment.—In order to obtain photographs that would permit of easy comparison with each other. it was decided to take Laue diagrams, the crystal throughout the test being held fixed relative to the X-ray beam.

Since the crystal tested was required to have an appreciable elastic range, tungsten appeared to be the most suitable material (the specimen used in the present experiment behaved elastically up to a normal tensile stress of about 90 tons per square in.). This material was obtainable as single crystals in wires up to 0·9 mm. diameter †. Finally, it was decided to use a tungsten single crystal wire of 0·2 mm. diameter, the small diameter being chosen both in order that the high stresses required should be easily obtained, and in order that the X-ray reflexions from the crystallographic planes should give sharp well-defined spots.

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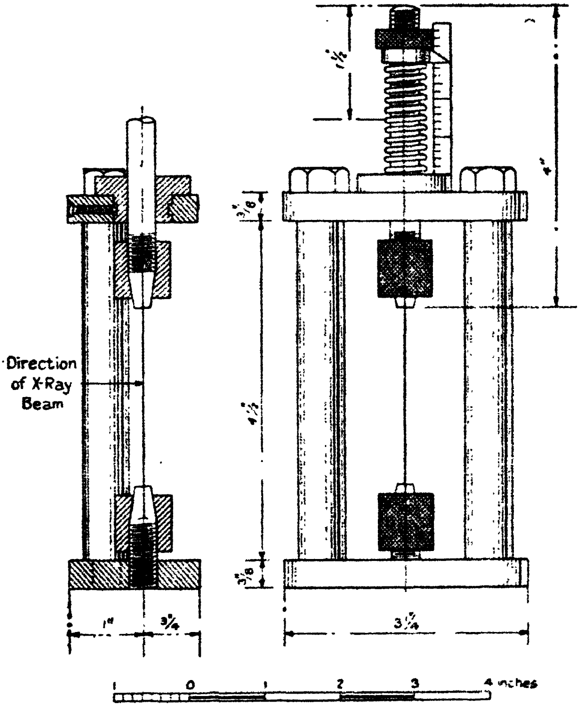
* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

† These single crystal wires were kindly supplied by the General Electric Company, to whom the authors wish to express their thanks.

A special straining apparatus was designed (fig. 1) in which the tensile load on the specimen was measured by a spring, previously calibrated against dead-weight loading. The length of the specimen used was approximately 3 inches between the chucks, and the specimen was examined approximately in the middle of this length, the direction of the X-ray beam being normal to the straining axis.

Fig. 1.



Apparatus for straining wires during X-ray analysis.

It was subsequently found that the portion of the specimen used was composed of more than one crystal; but at the section examined there was one main crystal with some indications of a second orientation. The changes of orientation to which reference is made below refer throughou to the main crystal. It is, of course, obvious that the presence of a small secondary crystal cannot have affected the shape of the spots due to reflexions from the main crystal.

Photographs were taken at stresses from 2 tons per sq. in. normal tension upwards, the increases in stress being made in steps ranging from 2 to 9 tons per sq. in. Each successive photograph was carefully inspected for any alteration in appearance ; but no definite change was observed until a stress of 97 tons per sq. in. had been reached, when it was obvious, from the large bodily movements of the spots, that the material had deformed plastically. A further photograph was taken at 104 tons per sq. in. and a final photograph at 1 ton per sq. in., and a comparison of these two showed that they were identical (Photos Nos. 23 and 24).

All the photographs at stresses up to and including 88 tons per sq. in. were then compared quantitatively, and the change of orientation between each pair of successive photographs was determined. In a visual comparison of the photographs allowance must be made for the fact that the distance of the photographic plate from the specimen was increased from 2·61 cm. to 3·00 cm. between the photographs taken at 34 and 36 tons per sq. in.

A complete record of all the photographs taken is given in Table I. below, while photographs Nos. 4, 20, 21, 22, 23, and 24 are reproduced in Pl. XXII.

The three rotations about the straining axis were all anticlockwise when viewed from above. Probably therefore they were not due to actual rotational movement of the straining head as the load was increased. On the other hand, the actual movements are so small that it is doubtful whether they lie outside the range of possible errors.

Conclusions.—Beyond the small bodily movements recorded above, no definite alteration in appearance of the Laue diagrams was observed until marked plastic deformation had occurred (Photo No. 22). The previous photograph (No. 21) showed a very slight broadening of the spots. If, as appears probable, this broadening was the beginning of the plastic broadening shown in photograph No. 22, then the elastic broadening, if it occurs, must be too slight to photograph successfully. If, on the other hand, the slight broadening in photograph No. 21 would have disappeared upon removal of the load, then it might be possible to obtain successful photographs; but, even if this is the case, the range in which the effect would be visible is extremely small (*e. g.*, in the present experiments it was not greater than 88 to 97 tons per. sq. in.), and very careful calculations would have necessarily to be made beforehand to ensure that, for the particular orientation of the specimen used, this narrow range of stress was not exceeded.

TABLE I.

No. of photograph.	Stress (tons per sq. in. normal tension).	Change of orientation from previous photograph.
4	2	—
5	4	None.
6	7	"
7	18	"
8	27	1° rotation about straining axis.
9	32	None.
10	34	"
11	36	Plate distance altered; otherwise no change.
12	38	None.
13	41	"
15	45	"
17	53	"
18	62	"
19	71	"
20	80	0·5° rotation about straining axis.
21	88	0·5° " " "
22	97	Large plastic movement.
23	104	Further plastic movement.
24	1	No change.

This work is an item in the research programme of the Sub-Committee on Elasticity and Fatigue of the Aeronautical Research Committee. The authors wish to express their thanks to the Committee for the opportunity to carry out this research and for permission to publish the results.

CXII. *The Determination of the Dielectric Constants of Imperfect Insulators.* *By* R. T. Lattey *and* O. Gatty *.

In determining the capacity of a condenser at high frequencies, neglect of the inductance of its leads may cause serious error; moreover, since no dielectric is a perfect insulator, it is also necessary to introduce corrections for the effects of leakage. No condenser can thus be supposed to be pure capacity, but consists of the parts shown in fig. 1. It can, however, be represented by either of the equivalent arrangements shown in figs. 2 and 3, where

$$\frac{K}{k}=\frac{1+p^{-2}k^{-2}x^{-2}}{1-p^2kl(1+p^{-2}k^{-2}x^{-2})}=1+p^2Kl+\frac{p^2K(R-r)^2}{1+p^2Kl}, \quad (1a)$$

$$R=r+\frac{x}{1+p^2k^2x^2}, \quad \ldots \ldots \ldots \quad (1b)$$

and

$$X=\frac{x^2(1-2p^2kl)+2xr+(r^2+p^2l^2)(1+p^2k^2x^2)}{x+r(1+p^2k^2x^2)}, \quad \ldots \quad (2a)$$

$$K'=\frac{k-l(p^2k^2+1/x^2)}{(r^2+p^2l^2)(p^2k^2+1/x^2)+1+2r/x-2p^2kl} \cdot \quad \ldots \quad (2b)$$

Fig. 1.

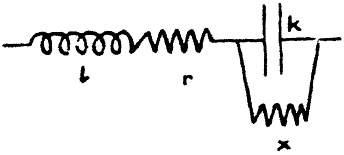


Fig. 2.

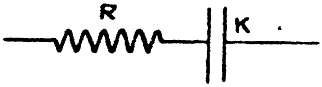
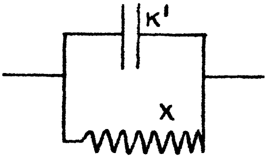


Fig. 3.



Bridge and resonance methods invariably admit of the direct evaluation of either K or K′. But if the effect of changing the dielectric in a condenser is to be used to deduce a dielectric constant, it will not be sufficient to correct K or K′ so as to obtain k, the capacity of the condenser system. For k must necessarily include a term k_l, which represents the capacity of the leads; every condenser has, too, a capacity relative to its surroundings which we may designate its "earth-capacity," and this part of the capacity is partly fixed and partly dependent on the dielectric in the condenser. Hence the total capacity actually measured will include that of the leads and the earth-capacity. If k_0 is the capacity of the condenser *in vacuo*, while A and B are constants and D is the dielectric constant of the fluid such that the measured capacity is k, then

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* Communicated by the Authors.

$$k = k_l + \mathrm{D}k_0 + \mathrm{AD}/(\mathrm{B}+\mathrm{D}).$$

The corrections to be applied to observed values may thus be regarded as:

(1) The capacity of the leads (see 16, 22, 28, 50, 55, 59, 63, 66, 78, 82).

(2) The inductance of the leads (see 75).

(3) The conductance of the dielectric or leakage (see 18, 22, 24, 25, 30, 35, 59, 62, 68, 74).

(4) The earth-capacity (see 22, 66, 75).

(5) Correction for the resistance of the leads.

Attempts to make allowance for these sources of error have been made by a variety of methods, some based on purely theoretical calculation and some on methods of substitution; but very few, if any, investigators have attempted to correct for all.

Considering first the evaluation of k, the capacity of the condenser system, equations (1 a) and (1 b) show that it will be practically always justifiable to neglect r. l, however, cannot be neglected even when it is small, as the following example will show. Two parallel straight wires, 1 mm. in diameter and 10 cm. each in length, at a distance of 3 cm. apart, have an inductance of 18×10^{-20} e.s.u. when carrying high-frequency currents in opposite directions. If these are used as leads to a condenser of 1000-cm. capacity, and if the frequency corresponds to a wave-length in air of 200 metres, then the effective capacity of the condenser will be

$$1000/0{\cdot}984 = 1016\,\mathrm{cm}.$$

If the condenser were then filled with a fluid whose dielectric constant was 2·3, its effective capacity would be 2300/0·9634, giving an uncorrected value for the dielectric constant of 2·35. If a frequency corresponding to a wave-length of 50 metres in air were used, the apparent dielectric constant would be given by

$$(2300/0{\cdot}415) \div (1000/0{\cdot}745) = 4{\cdot}13.$$

Thus it seems likely that neglect of the inductance of the leads may account for many of the supposed variations of dielectric constants with frequency which have been recorded by certain investigators and contradicted by others. Methods for evaluating l will be considered later.

Unless the leakage resistance x is very large and its equivalent R correspondingly small, it introduces certain very serious difficulties into Bridge methods for estimating capacities; for, if a balance is to be secured in such a case, either very large resistances must be used in the ratio arms or else the frequency must be very high. In the first case, the total current being small, the zero is correspondingly difficult to detect, and in the second case difficulties due to induction are increased and elaborate screening must be used. On high-frequency bridges a small total current is especially fatal, since the detector used, unlike the corresponding direct current galvanometer, is usually of such a type that its readings depend on the square of the current, and so correspond to a very low sensitivity in the neighbourhood of zero.

The alternative is to use "tuned circuit" methods, and as these depend on the selection of a position of maximum current, they can be made very sensitive. It is usual to adjust so that the current in the circuit is a maximum, *i. e.*, so that p^2KL (fig. 4) is equal to unity; the true capacity of the condenser system must then be found by equation (1 *a*). The usual procedure is to adjust the circuit by means of a well-insulated variable condenser K_1, and then to connect the unknown capacity in parallel with the variable capacity and to readjust the latter until resonance is again obtained (fig. 5). The condition for this is that

$$K + K_1 = K_0 \frac{1 - K_1/K_0}{1 - K_1/K_0 - p^2 K_0 K_1 \rho}, \quad . \quad . \quad (4)$$

where ρ is the apparent resistance of the condenser system and is given by

$$\rho = \frac{RK^2}{(K + K_1)^2 + p^2 K^2 K_1^2 R^2}. \quad . \quad . \quad . \quad . \quad (5)$$

K_0 is the value of the variable condenser when adjusted for resonance in the absence of K, while K_1 is the corresponding value after introducing K.

As before, K is not the true value of the unknown capacity, but that given by equation (1*a*). Moreover, K_1 and K_0 are not the true capacities of the variable condenser, since the inductance of its leads cannot be neglected at high frequencies. The scale readings must be corrected to give the effective capacities of the variable condenser, and these values be substituted in equations (4) and (5). The correction is effected by equations (1*a*) and (1*b*), putting $R-r=0$, i. e. $x=\infty$.

Observations made by the maximum current method thus require a considerable amount of correction in order to obtain the true value of the capacity of a condenser. The evaluation of the correction for resistance can be made by a method worked out by one of us (35); but on the whole it seems preferable to seek a method which does not involve so much correction. This is found in the method of tuning for maximum difference of a potential described below. It might be described as "Voltage Tuning," in contrast to the more usual "Amperage Tuning *."

Fig. 4.

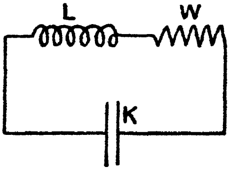
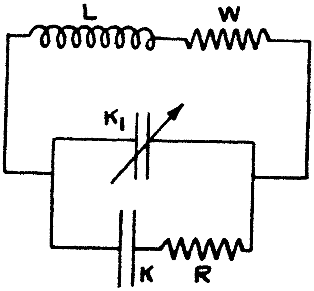


Fig. 5.



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* After the theory of voltage-tuning had been worked out by us and while the experimental part of this work was in progress two papers appeared which showed that, in broad outline, our views had been anticipated.

Jezewski (*Zt. f. Phys.* xlviii. 1928, p. 123) showed that voltage resonance at the terminals of a leaky condenser is independent of the leakage-resistance, but he did not examine in any detail the methods for detecting the point of resonance, nor did he consider the effect of the inductance of leads.

Kniekamp (*Zt. f. Phys.* li. 1928, p. 95) evolved the same theory, and applied it to finding the dielectric constants of solutions of sugar and of urea in water, measuring the voltage at the condenser terminals by means of an idiostatic thread electrometer.

The first suggestion of the theorem seems to have come from Tank (*Phys. Zt.* xvii. 1916, p. 114), but his statement is made without detail either mathematical or experimental.

In order to determine the Potential Difference between the terminals of a condenser it is necessary to connect them to something equivalent to a voltmeter. Investigation of the conditions favourable to maximum sensitivity shows that this voltmeter should have a low resistance and should therefore be coupled to the circuit through a condenser rather than through an inductance. For high-frequency work the only practical galvanometers depend on heating effects, and must therefore have some resistance; denoting this by G, it is required to find its optimum value. The circuit may be represented schematically by fig. 6*a* or 6*b*, and the condition for maximum current in G is

Fig. 6*a*.

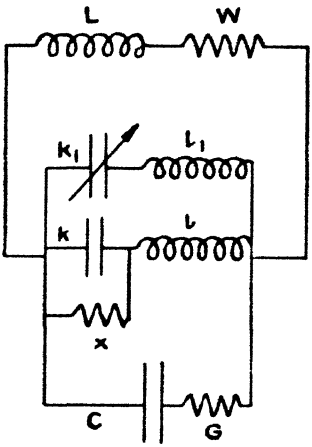
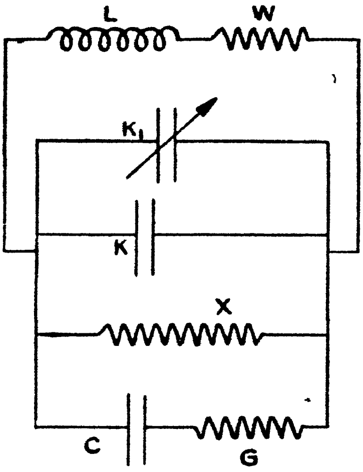


Fig. 6*b*.



$$K_m + K + \frac{C}{1+p^2C^2G^2} = K_0 + \frac{C}{1+p^2C^2G^2} = \frac{L}{r^2+p^2L^2}, \quad (6)$$

where K_0 is the value of the variable capacity giving maximum current in G when K and X are absent, and K_m is the corresponding value when K and X are present.

Neglecting the resistance of the condenser leads, equations (2*a*) and (2*b*) become

$$X = x(1-p^2kl)^2 + p^2l^2/x, \quad \ldots \ldots \quad (7a)$$

$$K' = \frac{kx^2(1-p^2kl)-l}{x^2(1-p^2kl)^2+p^2l^2} = \frac{k(1-l/kxX)}{1-p^2kl}, \quad . \quad (7b)$$

and these approximate to

$$X = x(1-p^2kl)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

$$K = k/(1-p^2kl) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8b)$$

for all values of p, k, l, x which are likely to occur in practice. Thus K is independent of x for all practical purposes, and by tuning for maximum voltage the necessity for applying a correction for conductance in the dielectric is abolished.

If we denote the current observed in G when $K_1 = K_m$ by I_m, and the current when K_1 is detuned by an amount $(K_m - K_1)$ by I_1, it may be shown that

$$\left(\frac{I_m}{I_1}\right)^2 = 1 + \left[\frac{p(K_m - K_1)}{\frac{1}{X} + \frac{W}{W^2+p^2L^2} + \frac{p^2C^2G}{1+p^2C^2G^2}}\right]^2, \quad . \quad . \quad (9)$$

from which it is clear that

$$\frac{1}{pX} + \frac{W}{p(W^2+p^2L^2)} + \frac{pC^2G}{1+p^2C^2G^2}$$

should be small so as to give sharp tuning. For values that are likely to occur in practice this expression approximates to

$$\frac{1}{pX} + \frac{W}{p^3L^2} + pC^2G \quad \text{or} \quad \frac{1}{pX} + pW(K+K_m+C)^2 + pC^2G,$$

and it is thus clear that W, C, and G should all be small. When X is comparatively small it may be advantageous to increase the frequency p; but this should be avoided, if possible, since it increases the correction terms indicated by equation (8b).

If the ratio (Voltage induced in Circuit) to (Current in G) be denoted by Z, then the minimum value of Z is

$$Z_m = \frac{1}{pC}\left(\frac{1}{X} + \frac{W}{W^2+p^2L^2} + \frac{p^2C^2G}{1+p^2C^2G^2}\right)$$
$$\sqrt{W^2+p^2L^2}\,\sqrt{1+p^2C^2G^2}\,; \quad (10)$$

and, as it is clearly desirable that this should be small, G may be taken as variable in order to find a minimum value for Z_m. This gives

$$\frac{1}{X} + \frac{W}{W^2+p^2L^2} = \frac{p^2C^2G}{1+p^2C^2G^2}$$

or approximately

$$\frac{W}{p^2L^2} \equiv p^2W(K+K_m+C)^2 = p^2C^2G,$$

or

$$\frac{K+K_m+C}{C} = \sqrt{\frac{G}{W}}.$$

This was checked experimentally, using air condensers for which X may be taken as infinite. G was a heating wire whose resistance was known to be about 8 ohms. The wave-length in air was 157 metres, corresponding to a frequency 12×10^6. The maximum value of C available was 0·5 MMF. and that of K 1·0 MMF. W was made small and was estimated to be of the order of 1 ohm. Hence approximately

$$pCG = 12\times10^6\times0{\cdot}5\times10^{-9}\times8 = 0{\cdot}048,$$

also

$$pL = [p(K+C)]^{-1} = [12\times10^6\times1{\cdot}5\times10^{-9}]^{-1} = 55,$$

and W^2 is thus to be neglected in comparison with p^2L^2. For practical purposes the formulæ then assume the approximate forms :

$$Z^2 = \frac{L^2}{C^2}\left[\left(p(K+C)-\frac{1}{pL}\right)^2+\left(p^2C^2G+\frac{W}{p^2L^2}\right)^2\right]$$

$$= \frac{(K-K_m)^2+p^2(C^2G+(C+K_m)^2W)^2}{C^2(C+K_m)^2}$$

and

$$\frac{K-K_m}{[(I_m/I)^2-1]^{1/2}} = p\{C^2G+(C+K_m)^2W\}.$$

A transmitter was kept going as constantly as possible, and C was varied by steps of 0·05 MMF. from 0·115 to 0·465, and the values of X and the function

$$(K-K_m)/\sqrt{(I_m/I)^2-1} = \phi$$

determined at each step ; from the last equation the values of G and and W can be calculated, giving G=10·19 and W=1·50 ohms.

The condensers used for this experiment were not those used in subsequent work and had not been carefully calibrated; consequently no very high order of accuracy can be expected. Taking the value of $C+K_m$ as 0·9375 the formula for calculating ϕ becomes

$$12\times10^6(10{\cdot}19\,C^2+1{\cdot}50(0{\cdot}9375)^2),$$

and it will be seen from column 6 that this gives quite reasonable concordance with observation. Theory indicates that I_m should be a maximum when

$$C = (C+K_m)\sqrt{W/G} = 0{\cdot}9375\,(1{\cdot}50/10{\cdot}19)^{1/2} = 0{\cdot}360.$$

Table I. also bears this out. Moreover, since

$$Z_m = E/I_m = p\{C^2G + (C+K_m)^2W\}/C(C+K_m)$$
$$= \phi/C(C+K_m),$$

the value of $I_m \times \phi/C$ should be constant, as is indicated by column 7.

Similar results were obtained at other frequencies, all bearing out the correctness of the formulæ on which the theory of the method described in this paper depends.

TABLE I.

				ϕ.		
C.	I_m^2.	K_m.	$C+K_m$.	found.	calc.	$I_m \times \phi/C$.
0·115	30	0·823	0·940	0·0181	0·0174	0·861
0·165	56	0·774	0·939	0·0195	0·0195	0·885
0·215	78	0·724	0·939	0·0216	0·0215	0·886
0·265	92	0·675	0 940	0·0246	0·0244	0·892
0·315	98	0·624	0·939	0·0269	0·0279	0·843
0·365	99·5	0·570	0·935	0·0310	0 0321	0·847
0·415	97	0·515	0·930	0·0362	0·0369	0 859
0·465	89	0·453	0·918	0·0426	0·0423	0·865

In the preceding paragraphs we have treated the capacities used in terms of their equivalents when inductance of leads and faulty insulation are absent. It now becomes necessary to develop means for evaluating the constants involved in equation (1) ; the details of a practical circuit are indicated in fig. 6*a*, where the subscript 1 indicates the calibrated variable condenser, while *k*, *l*, and *x* refer to the capacity inductance and leakage resistance of the unknown capacity. The circuit is assumed to be so loosely coupled to the transmitter that mutual inductance may be neglected.

Evaluation of Inductances l *and* l_1.

If the unknown capacity can be given two values successively without changing its leads, then, if these are k_1'

and k_2' and the settings of the variable condenser are k_0, k_1, and k_2 in absence, in presence of k_1' and of k_2' respectively, it follows from equation (1) that

$$\frac{1}{k_1'}-\frac{1}{k_2'}=\left(\frac{1}{\Delta_1}-\frac{1}{\Delta_2}\right)(1-p^2k_0l_1)^2, \quad . \quad . \quad (11)$$

where $\Delta_1=k_0-k_1$ and $\Delta_2=k_0-k_2$. If therefore the frequency is varied, the product $[\Delta_1\Delta_2/(\Delta_2-\Delta_1)]^{1/2}$ should be a linear function of p^2k_0, from which l_1 and the left-hand side of equation (11) can readily be obtained.

Two methods were tried for changing k' without changing l. In the first a condenser with rotating vanes was used (an ordinary wireless condenser), set first at one end of its scale and then at the other. The frequency and the main inductance of the circuit (L) were varied over a wide range. In the second method a condenser was used, filled first with water and then with nitrobenzene (any two fluids of which one has about twice the dielectric constant of the other would do). The first method has the possible disadvantage that the inductance of the leads may perhaps change when the vanes are rotated; the second method has the disadvantage that it is not easy to repeat the sequence of frequencies used with absolute accuracy, and there is also a possibility that the dielectric constant of one or both of the fluids used may be a function of the frequency; this is however unlikely at the frequencies used by us. The results of both methods were in substantial agreement, and were subsequently checked by the use of the two small mica condensers, which could be attached by leads so short that their inductance was clearly negligible.

Since wave-meters are more usually calibrated in wave-lengths than in frequencies, it is more convenient to find values for $4\pi^2c^2l_1$ than for l_1, since $p^2l_1=(4\pi^2c^2l_1)/\lambda^2$.

The results (Table II.) obtained with the rotating condenser may be quoted as an example.

If the condenser to be tested is now inserted and values of Δ obtained at various frequencies and various values of k_0, then l can be evaluated in the form

$$p^2l=1/k'-(1-p^2k_0l_1)^2/\Delta-p^2l_1(1-p^2k_0l_1). \quad . \quad (12)$$

The true capacity (k') of the unknown condenser filled with any given dielectric is then to be found by the equation

$$\frac{\Delta}{k'}=(1-p^2k_0l_1)^2+p^2\Delta(l+l_1(1-p^2k_0l_1)). \quad . \quad (12a)$$

TABLE II.

λ.	k_0.	Δ_1.		Δ_2.		$[\Delta_1\Delta_2/(\Delta_2-\Delta_1]^{\frac{1}{2}}$	
		obs.	calc.	obs.	calc.	obs.	calc.
70·5	472·7	31·63	31·57	187·31	188·46	6·169	6·154
78	544·5	31·64	31·08	185·02	185·60	6·178	6·109
94	1014·6	30·10	30·09	174·90	173·50	6·030	6·030
107	832·4	32·08	32·72	187·03	186·92	6·223	6·293
129	301·3	36·17	36·30	204·81	205·34	6·628	6·636
191	994·7	35·22	35·58	197·62	198·76	6·547	6·578
221	526·1	37·19	36·69	205·03	204·43	6·740	6·685
Inf.	—	—	37·36	—	206·63	—	6·749

As an example we may take a condenser filled with water at 16° C.

TABLE III.

λ.	k_0.	Δ.	k'.
72	512·3	220·95	225·4
75	549·3	217·4	224·65
87	491·9	229·4	230·7
89·5	904·2	209·2	233·5
106	793·9	217·35	230.1
116·5	1036·0	211·8	230·1
159	614·5	226·6	229·25
174	770·4	226·0	230·3

It will be seen that, while the values of Δ range between 209 and 229, the value deduced for k' only varies from 224 to 231. (This variation of about 3 per cent. is probably due partly to failure in securing absolute constancy of temperature and partly to the fact that the necessity for always filling a condenser to exactly the same depth was not fully realized at the time when these preliminary observations were made.)

Relation between Capacity observed and Dielectric Constant.

It has already been pointed out that the capacity actually measured will include that of the leads and the earth capacity of the condenser; this may be expressed by $k_l + k_0 D + AD/(B+D)$. If k_0 is large, k_l and A may be neglected or their effects minimized by basing calculations on the difference between two settings of a variable condenser.

But if imperfect insulators are to be used, then k_0 cannot be very large, since this would make the leakage conductance correspondingly great and so make observations very difficult.

Our procedure therefore was to find the dielectric constants of a few good insulators by using a variable condenser of large capacity, and then to calibrate our small condensers by the use of these fluids. The liquids actually used were carbon tetrachloride, chloroform, and a mixture of these; the variable condenser was that referred to in Table II. Our small condensers were then tested with air, the above liquids, methyl alcohol, nitrobenzene, and water in them. This gives four cases in which the dielectric constant is known, and four others about which all that is known is that the condensers must be consistent with one another. In this way the following values were deduced:—

Condenser.	X.	Y.	Z.
k_l	0·26	0·26	0·26
A	8·345	6·23	7·85
B	0·94	0·94	0·94
k_0	11·248	6·368	11·266

Assuming that, as all three were of the same form and differed only in length, the edge-correction would be the same for all, then, from their dimensions, X and Z should be equal, and each greater than Y by 4·51 e.s.u. The experimental value of about 4·89 is satisfactory when we bear in mind that the units in which our condensers were graduated were only approximate centimetres.

The condensers X, Y, and Z, with which the main series of observations were made, were of copper silver-plated; this proved satisfactory for certain liquids including cold water; but when hot water was used, the metal was attacked and became visibly tarnished, the conductivity of the water was markedly increased, and its dielectric constant lowered. This gave an apparently different temperature coefficient from that of other observers; but as subsequent observations, using pure silver plates, have given results in accordance with those usually accepted, it is clear that the apparent anomaly was due to a change in composition of the dielectric.

The condensers were in the form of concentric tubes held in place by rods of glass.

Our calibrated condenser consisted of a series of fixed plates which could be brought into circuit by inserting plugs, as is usually done in resistance boxes ; in parallel with this was a condenser with rotating vanes giving a range of capacity rather greater than that of one plate.

Temperature Coefficients of Dielectric Constants.

For those dielectrics which are not much affected by temperature a simple linear formula is satisfactory ; but those dielectrics like water and the alcohols which have comparatively large dielectric constants, are more profoundly influenced by temperature, and the changes so brought about cannot be represented by a linear law. For such cases two types of formula have been suggested : (i.) by Abegg (1) this may be written $\log D = \log D_0 - \alpha(\theta - 273)$, and (ii.) by Adams (2) $\log D = \log D_0 - n . \log(\theta/273)$. In those cases in which we have tested these formulæ we have invariably found Abegg's quite as good as Adams's and in some cases better ; it is moreover simpler, and we therefore propose to express all our results in terms of it, using decadic logarithms.

RESULTS.

1. *Benzene* *.—A specimen purified by Mr. R. W. Knight for use in some cryoscopic work was tested between 14° and 71° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	2·2934	0·265
Cauwood and Turner (6)	2·2768	0·2865
Hasenöhrl (23)	2·1547	0·449
Negreano (41)	2·1939	0·526
E. H. L. Meyer (38)	2·2737	0·2985
Ratz (51)	2·2805	0·2935
Lange (34)	2·3033	0·330
Grützmacher (20)	2·3109	0·257
Graffunder (18)	2·3137	0·366
Stranathan (66)	2·3223	0·418
Tangl (67)	2·3326	0·403
Isnardi (27)	2·3516	0·458
Palaz (45)	2·3862	0·557
Schulze (59)	2·6139	2·253

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* While this paper was in the press there appeared another by Hartshorn and Oliver (Proc. Roy. Soc. cxxiii. p. 664 (1929) in which they give 2·282 as the dielectric constant of benzene at 20° C.

Benzene (*cont.*).

Temp.	Authors.	Their D.	Our D.
12·7	Landolt and Jahn (33)............	2·2074	2·276
13·4	„ „ „	2·1977	2·275
14·2	Silberstein (61)	2·07	2·274
14·5	Landolt and Jahn (33)............	2·2221	2·273
15	Kerr (31)	2·28	2·2725
	Michaud and Balloul (40)	2·28	
	Saint-Antoine (54)	2·23	
16	Watson (75)	2·286	2·271
17	Siivola (60)	2·258	2·270
	Drude (10)	2·255	
	Veley (72)	2·27	
	Nernst (42)	2·255	
18	Turner (71)	2·288	2·268
	Errara (14)	2·285	
	Philip (47)	2·242	
19	Drude (10)............................	2·26	2·267
19·6	Tomaszewski (69)	2·218	2·266
20	Linebarger (36)......................	2·249	2·266
	Philip and Haynes (48)	2·29	
25	Harris (22)...........................	2·2485	2·259
	Williams and Krchma (78)	2·283	
	Sayce and Briscoe (55)	2·23	
25·5	„ „ (56)	2·239	2·258
80·15	Grimm and Patrick (19)	2·17	2·184

2. *Carbon tetrachloride.*—A good commercial sample tested between 15° and 71° C.

Authors.	D_0.	$a\times10^3$.
L. and G.	2·2655	0·461
Grützmacher (20)	2·2179	0·2755
Stranathan (66)	2·2610	0·399
Isnardi (27)........................	2·3592	0·3175

Carbon tetrachloride (*cont.*).

Temp.	Authors.	Their D.	Our D.
12°·5	Veley (72)	2·049	2·236
17	Drude (10)	2·18	2·225
18	Turner (71)	2·246	2·2225
	Franke (16)	2·227	
	Schulz (59)	2·248	
20	Linebarger (36)	2·241	2·218
21·3	Bugarsky (4)	2·241	2·215
23	Grimm and Patrick (19)	2·2	2·211
25	Sayce and Briscoe (55)	2·20	2·206
	Williams and Krchma (78)	2·230	
	Harris (22)	2·1873	
76·7	Grimm and Patrick (19)	2·10	2·088

3. *Chloroform.*—A good commercial sample tested between 14° and 58° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	5·372	1·736
Ratz (51)	5·1035	1·680
E. H. L. Meyer (38)	5·148	1·802
Tangl (67)	5·1865	1·460
Smyth and Morgan (64)	5·2145	1·7635
Cauwood and Turner (6)	5·310	1·768
Isnardi (27)	5·317	1·703
Grützmacher (20)	5·398	1·437

Temp.	Authors.	Their D.	Our D.
5°	Schulze (59)	5·646	5·2655
15	Joachim (30)	5·06	5·059
	Thwing (70)	3·95	
17	Drude (10)	4·95	5·019
	Kerr (31)	4·85	
17·8	Ortvay (44)	5·042	5·003
18	Turner (71)	5·2	4·999
	Walden (73)	4·95	
	Philip (47)	4·864	
	Nernst and Lerch (43)	5·1	

Chloroform (*cont.*).

Temp.	Authors.	Their D.	Our D.
20	Schulze (59)	4·857	4·959
	Lineberger (36)	5·132	
22	Nernst (42)	5·14	4·920
24	Carman (5)	5·6	4·8805
25	Williams (78)	4·770	4·851
	Harris (22)	4·642	
	Sayce and Briscoe (55)	4·79	
26	Schulze (59)	4·540	4·8415
61·2	Grimm and Patrick (78)	4·23	4·206
	Cauwood and Turner (6)	4·130	

4. *Mixture of Chloroform and Carbon tetrachloride* containing 38·80 per cent. by mass of chloroform.

$\log D = \log 3{\cdot}2931 - 0{\cdot}001015\,(\theta - 273)$. Interpolation of Grützmacher's values gives

$\log D = \log 3{\cdot}2435 - 0{\cdot}000857\,(\theta - 273)$.

5. *Methyl alcohol.*—A specimen kindly prepared for us by Sir H. B. Hartley. Investigated between 12° and 59° C. $D_0 = 37{\cdot}0635$, $\alpha = 0{\cdot}002415$. Compare Abegg and Seitz (2), who found $D_0 = 34{\cdot}735$, $\alpha = 0{\cdot}002302$.

Temp.	Authors.	Their D.	Our D.
0°	Walden	34·9	37·06
13·4	Landolt and Jahn (33)	34·86	34·40
15	Thwing (70)	34·05	34·10
	Joachim (30)	36·17	
	Walden	36·17	
16	„	32·4	33·91
	Drude (10)	32·5	
17	„ „	33·2	33·72
18	Harrington (21)	33·78	33·53
	Rudolph (52)	31·5	
	Falkenberg (15)	33·0	
	Potapenko (49)	32·0	
24	Carman (5)	35·5	32·43

6. *Nitrobenzene.*—A good commercial sample dried and redistilled. Investigated between 15° and 70° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	39·338	2·283
E. H. L. Meyer (38)............	36·235	2·019
Abegg and Seitz (2)	40·31	1·893
Lange (34).......................	42·175	2·485
Jezewski (29)....................	37·46	1·972

Temp.	Authors.	Their D.	Our D.
15°	Thwing (70)	32·19	36·355
	Kerr (31)	35·03	
	Joachim (30)	36·45	
16	Philip (47)	37·14	36·165
18	Errera (13)	35·67	35·785
	Turner (71)	36·45	35·785
20	Kerr (31)	33·91	35·41
25	Williams and Ogg (80)...........	36·10	34·495
	Harris (22)........................	34·093	
210·35	Grimm and Patrick (19)	15·61	12·99

7. *Nitromethane.*—Purified by Mr. C. P. Wright under the direction of Sir H. B. Hartley; boiling-point 101·15° C. Investigated between 12° and 92° C.

$$\log D = \log 40{\cdot}88 - 0{\cdot}00189\,(\theta - 273).$$

Comparison of Experimental Values in Condensers X, Y, and Z with those calculated by the above Formulæ for Nitromethane.

Temp.	λ.	X.	Y.	Z.	Calc.
12°	90·0	38·55	—	—	38·799
	76·6	—	38·64		
	80·34	—	38·87		
	137	—	38·68		
	131	—	39·02		
12·5	90·0	—	39·00	—	38·715
	102·7	38·72	—	38·52	

Nitromethane (*cont.*).

Temp.	λ.	X.	Y.	Z.	Calc.
12·9	108·2	38·67	—	38·45	38·647
	118	38·81	38·535	38·50	
	71·7	38·56	—	38·61	
14	96·2	38·35	38·48	38·34	38·446
16	193	38·25	38·22	38·13	38·129
	217·8	38·06	38·18	38·03	
	144	38·09	—	38·00	
	141	—	38·17		
	90·6	37·95	38·05	38·04	
17	115·6	38·26	38·14	38·27	37·964
22	96·2	37·03	37·245	37·08	37·147
		37·26	37·11	36·87	
29	96·2	35·935	35·695	35·81	36·033
40·4	96·2	33·98	34·00	33·985	34·288
48·75	96·2	33·00	32·89	32·86	35·064
61	96·2	31·285	31·29	31·14	31·349
71	96·2	30·06	30·01	29·81	30·014
81·5	96·2	28·77	28·77	28·56	28·673
91	96·2	27·67	27·75	27·43	27·512
			27·85	27·47	

Temp.	Authors.	Their D.	Our D.
15°	Thwing (70)...	56·36	38·24
19	Schlundt (58)	40·4	37·58
20	Walden (71)............................	38·8	37·415
25	Grimm and Patrick (19)	39	36·61
101·7	,, ,, ,, ...	27·75	26·22

8. *Water.*—As was mentioned earlier, it was not practical to find the temperature coefficient for water in condensers with plated electrodes; but the results with cold water were in good accord with those of Kockel (32), Coolidge (9), Franke (16), Drude (10), and Ratz (51). These all agree substantially in giving the equation:

$$\log D = \log 87{\cdot}73 - 0{\cdot}0020095\,(\theta - 273).$$

How good is the agreement may be seen from the following table :—

Dielectric Constant of Water.

Temp.	Kockel.	Coolidge.	Franke.	Drude.	Ratz.	Calc.
0°	88·04	88·42	—	87·28	88·00	87·73
10	83·71	84·31	85·09	83·81	83·68	83·76
20	79·69	80·49	80·51	80·04	78·81	79·975
30	75·88	75·75	—	76·30	75·80	76·36
40	72·34	73·24	—	72·93	—	72·905
50	69·02	—	—	69·93	—	69·61
60	65·91	—	—	67·22	—	66·46
70	63·04	—	—	64·54	—	63·46
80	60·36	—	—	61·91	—	60·59
90	57·84	—	—	—	—	57·85
100	55·30	—	—	—	—	55·23

From measurements made at one temperature, only those which agree with the above formula need be quoted here.

Temp.	Authors.	Found.	Calc.
17°	Palmer (46)	81·40	81·09
	Weichmann (76)	80·28	
	Colley (8)	80·26	
	Heerwagen (25)	80·88	
	Holborn (26)	81·51	
	Wildermuth (77)	80·5	
	Abegg (1)	80·84	
17·5	Nernst (42)	80·3	80·905
18	Nernst and Lerch (43)	81·7	80·72
	Sack (53)	80·85	
	Errera (14)	81·02	
	Turner (71)	81·07	
18·7	Cohn and Zeeman (7)	80·19	80·455
19	Mazotto (37)	81·00	80·345
20·75	Heerwagen (25)	79·56	79·70
21·15	Cohn and Zeeman (7)	78·88	79·54
22·2	„ „ „	79·8	79·165

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CXIII. *The Rare Earths associated with Uraninites.*

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THE fact is well known that seldom are radioactive minerals free from rare earths, or rare earth minerals lacking in an appreciable content of uranium or thorium. Chemically, both uranium (uranous) and thorium bear close resemblances to the rare earths ; and this similarity might be thought sufficient to account for their association with the cerium and yttrium groups of elements. Our knowledge, however, is very inadequate, and the present investigation was undertaken with the object of studying more closely than has been done heretofore the nature of the rare earths associated with minerals consisting essentially of uranium oxides.

Very complete analyses of uraninites from a large number of different sources were made about 1890 by Hillebrand (Amer. Journ. Sci. xl. p. 384, 1890 ; xlii. p. 390, 1891) on the material then available. Most of these contained several per cent. of thoria and from 1 to 10 per cent. of rare earths. His analyses show, in all cases where his rare-earth group was divided, that the yttrium subgroup (*i. e.*, yttrium and atomic numbers 66 to 71, or the more feebly basic earths, and those with highest atomic weight) represented a considerable proportion, often much the larger proportion, of the earths present.

If all the analyses now available are examined it will be noticed that the older uraninites are richer in thorium and the rare earths than the younger, though there is no apparent proportionality between the rare earth and lead content. The result is sufficiently striking in the case of the rare earths to warrant an investigation as to whether any evidence can be deduced to show that there has been a growth of the earths in the course of time. In many cases it is obvious that the rare earth is present in such a large proportion as to make fairly certain that it was an original constituent of the mineral, and so the minerals investigated should be those having a minimum rather than a maximum of rare earth.

Isolation of the Rare-Earth Group.

The general procedure was to attack the powdered mineral with hot nitric acid and evaporate to dryness. The residue was taken up in water and any insoluble remainder removed. Lead and radium were then precipitated as sulphates, and following this the H_2S precipitate was removed. Excess of hydrofluoric acid was then added. This caused precipitation of thorium and the rare earths. The thorium was best removed by adding to a dilute boiling solution of the mixed chlorides a sufficiency of sodium thiosulphate, causing a basic thorium thiosulphate to precipitate. The earths were finally obtained pure by repeated precipitations as oxalates and ignition.

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* Communicated by Prof. Fredk. Soddy, F.R.S.

TABLE I. Uraninites examined.

No.	Locality.	Rare-earth content.	Age*.
		Per cent.	
1.	Joachimstal, Czecho-Slovakia.	·0	205×10^6 years.
2.	Katanga, Belgian Congo.	·15	575
3.	S. India.	·7	900
4.	Morogoro, Tanganyika Territory.	·1	640
5.	Cornwall.	·17	220
6.	Norway.	1·0	900

No. 1. The actual pitchblende was not examined, but a rare-earth residue obtained from the radium factory. The analyses on record show no rare-earth content, but some is found on large-scale work.

No. 2. The earth from 1 kg. of average ore was available for examination.

No. 3. The specimen was about half black pitchblende and about half weathered to a soft yellow earth.

No. 4. The sample was a fine compact black pitchblende with which was some yellow Rutherfordine and a little mica.

No. 5. The pitchblende contained copper and arsenical pyrites, galena, and much titanium.

No. 6. The material was crystalline Bröggerite of high degree of purity.

Methods of Examination.

The arc spectrum of the oxides and the absorption spectrum of a chloride solution were examined in each case.

Part of the work was done on a Féry spectrograph and part with a large Littrow spectrograph, the region 2500 to

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* From Holmes, 'The Age of the Earth' (Ernest Benn, Ltd., 1927).

3500 A.U. only being photographed with the latter instrument in the examination of the arc spectra. Spectrograms from the Féry instrument were projected with a 12·5 times enlargement against a scale of wave-lengths ruled to suit. The error in reading the wave-lengths below 3500 Å.U. did not amount to more than ·1 or ·2 Å.U.*.

Photos from the larger instrument were projected so as to obtain the same dispersion, and comparison with prints from the smaller instrument could then be made directly. It was not difficult to identify almost all the lines with one or other of the rare-earth elements. Some of the rare earths give easily identified lines, even when present in very small quantity. These, fortunately, are the elements which usually cannot be identified by their absorption spectra, viz., Yt, Yb, Eu, Gd, La, Lu, Sc. The elements Dy, Ho, Tm, Er, Sm, Tb, and Ce give less prominent lines, whilst Pr and Nd give no lines, at any rate in the ultra-violet, which enable them to be distinguished with certainty in a mixture unless they form a large proportion of the whole. They may, on the other hand, be detected very delicately by their absorption spectra.

A chloride solution of each earth was prepared by dissolving the oxide in hydrochloric acid and making up the solution to a volume which represented ·4 gm. E_2O_3 per c.c. Absorption photographs were taken through 1 cm. thicknesses of this solution, using a source of continuous emission. In some cases a further photograph was taken, using a 5-cm. layer. Each of the coloured earths possesses at least one band fairly well distinct from strong bands of all other elements, which made it possible to identify it in the crude mixture.

Results.

An attempt was made to obtain an approximate estimate of the amount of each earth present by selecting a weak isolated band, and from the data of other workers determining what concentration its presence indicated for that earth in the solution. The bands found useful and the results arrived at are shown in Table II. The 40-per-cent. oxide-chloride solution employed probably represented a strength of about 8 times normal. The estimate is for Joachimstal earths, and for comparison the amount of the various earths found on actual fractionation is also given as accurately as possible.

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* See O. Free, Phil. Mag. lx. p. 950 (1926), for description of this method.

In the material which was fractionated, lanthanum and cerium had been removed previously.

An approximate estimate of the actual amount of rare earth present in the six samples of uraninite is found in Table I. "Uraninites examined" (p. 1006). It will be seen that the two oldest samples contain considerably higher amounts than the others. These two (Norwegian Bröggerite and Indian pitchblende) were also the only ones to contain appreciable quantities of thorium. The former held 1 per cent. and the latter ·7 per cent. The next highest thorium-content was in the Cornish pitchblende, and this, it will be seen, though young, had the third greatest rare-e content.

Table II.

Element.	Band.	Amt. in 8N solution.	Per cent. on fractionation.
Praseodymium.	4441	N/2	4
Neodymium.	6250	N	16
Samarium.	4070	N/2	6
Europium.	3950	N/5	2
Gadolinium and terbium.	—	—	7
Dysprosium.	3865	N/2	4 ?
Holmium.	6430	N/10	1 ?
Erbium.	6536	N/3	56
Yttrium.	—	—	
Ytterbium.	—	—	4

Scandium.—This earth was found to constitute at least 10 per cent. of the rare earth present in Katanga pitchblende. The element accompanies thorium in the thiosulphate method of separation from the rare earths, and was detected spectroscopically in the thorium from Indian pitchblende on adding to its solution ammonia and ammonium tartrate and boiling. Only 2 milligrams, however, were obtained. None was thus separable in the other cases, but in every case some of the very highly sensitive lines were detectable in the arc spectrum. They were strongest in the Morogoro earth and seen next best in Bröggerite.

Europium.—The distribution of this element was found to be of considerable interest. It may be detected by its arc spectrum when only the minutest traces are present, and ordinarily, with the exception of illinium, it is least abundant of the rare-earth elements. It was found to be virtually absent in the Indian pitchblende, and in the Bröggerite there was only a very minute quantity. On the other hand, the Katanga and Joachimstal pitchblendes must be among the richest sources of the element yet found. Urban (*J. chim. phys.* iv. p. 232, 1906) has already remarked upon its abundance in pitchblende, presumably from Joachimstal, estimating it as greater than the gadolinium- and almost as great as the samarium-content. Whilst the present work does not quite bear out this proportionality, it has been found by actual fractionation of 300 grams of rare earths from Joachimstal residues that the content must approach 2 per cent. in the crude mixture. This may be compared with a content in monazite said not to exceed ·002 per cent. The europium absorption band at 3950 A.U. was observed in a 1-cm. layer of concentrated solution of the mixed earths, and from its strength a rather higher, but not dissimilar, estimate of its abundance was arrived at. The amount present in the Katanga earths appears from the absorption spectrum to be even greater, and the content in Morogoro earth is probably not widely different, though rather less than in the material from Joachimstal.

With regard to the other earths, it may be stated that the Cornish material was richest in cerium and the cerium group. Lanthanum was not present to any appreciable extent in Morogoro and Bröggerite earths, and the amount in the Indian earths was small. These three materials contained the highest proportions of yttrium. The Morogoro product in particular gave less indication of coloured earths than the others, the neodymium and praseodymium absorption bands being very weak. The oxides themselves were pale in colour. The amount of samaria in Joachimstal and Katanga earths was unusually high. In the Joachimstal material which was fractionated the amount was found to be 4 to 5 per cent., or equal to about one-third of the neodymium present. The proportions of the earths in this mixture, however, had been disturbed from the original by the extraction from them of the actinium and some of the most basic earths, and of ionium and some of the least basic earths. The remainder which was submitted to fractionation had consequently probably gained a little in richness in earths occupying a central position in the usual serial order of the elements. The estimate is also made on the cerium-free material, and cerium amounted to nearly 20 per cent. of the earth before its removal.

Gadolinium arc lines could be detected in all cases with ease, but owing to their sensitivity they do not afford much evidence of the amount present. The general absorption of the earths masked the absorption bands of gadolinium, which all lie in the ultra-violet, so that no use could be made of them in arriving at an estimate of the abundance. In the Joachimstal material, on fractionation about 6 per cent. was isolated. Terbium appears to be abundant in the Indian earths and scarce in the Katanga. This, it may be remarked, is just the reverse of what is found in the case of europium. The amounts present, however, are small and the evidence scanty. Dysprosium and holmium are relatively most abundant in Indian and Bröggerite earths. Of the remaining earths there is little that can be recorded. Yttrium with a little erbium constitutes at least 50 per cent. of the 300 grams of Joachimstal earths that were fractionated.

It is instructive to compare the above results with the work of Hauser and Wirth (*Ber.* xlii. p. 4443, 1909). They have made a study of the earths occurring in euxenites (yttrium columbo-titanites) and polycrases (yttrium columbo-tantalates), and find praseodymium and samarium to increase in abundance with the amount of titanic acid. Also thorium and titanium occur together, or not at all, in the columbates which they examined. The earths from Joachimstal, Katanga, and Morogoro appear to resemble extreme examples of the tantalic acid type. In the other three earths which contained either considerable titanium or thorium, the type corresponding, according to the views of Hauser and Wirth, appears dominant; and most markedly is this so in the Indian earths, where the thorium content is highest. No actual information with regard to the tantalum-content of the different minerals was obtained.

The mineral samarskite is said to be the best source of europium among the ordinarily available rare-earth minerals. This is a columbo-tantalate of rare earths with 10 to 15 per cent. of uranium oxides and very little thorium. Bearing in mind what has been said previously with regard to europium, it would appear to be a general rule that uranium and europium associate together in nature, but that thorium and europium do not.

Conclusions.—Enough has been said to make it clear that the earths of pitchblende show no features in common more than will be found amongst almost any six rare-earth samples taken at random from different minerals. It seems possible that the earths are not actually part of the uraninite in all cases, but are in reality derived from some associated mineral such as samarskite. Thus Hauser (*Ber.* xliii. p. 417, 1910) has described a mineral, plumboniobite, which is found together with the Morogoro pitchblende at Morogoro, and which is very rich in samarium and gadolinium. W. Markwald (*Zentr. Min. Geol.* p. 761, 1906) found 2 per cent. of rare earth in his analysis of Morogoro pitchblende—a much greater amount than the author has found in his very pure sample. However, the earths separated in the present investigation were remarkable, like the earths from Hauser's plumboniobite, in their lack of lanthanum, cerium, and didymium ; and the conclusion seems justifiable that in this instance the rare earth is an intimate associate rather than a genuine constituent of the pitchblende.

The rare earth in pitchblende is due to imperfections in the chemical or physical separations which have taken place during magmatic differentiation, or subsequent segregations. The greater amount of rare earth in very old uraninites may probably be accounted for as being due to a greater turbulence in the magma and greater volcanic acitvity 10^9 years ago than in more recent times.

In conclusion, I wish to acknowledge my debt of gratitude to Prof. Soddy for laboratory facilities provided during a large part of this work, and for his interest in it. It was undertaken at his suggestion, and largely made possible by the use of materials placed at my disposal by him.

CXIV. *The Acoustic Performance of a Vibrating Rigid Disk driven by a Coil situated in a Radial Magnetic Field*[*].

By N. W. McLachlan, *D.Sc., M.I.E.E., F.Inst.P.*[†]

Synopsis.

1. Analysis of System without Elastic Constraint.
2. ,, ,, with ,, ,,
3. Transient Solutions.
4. Acoustic Pressure on Disk and Power radiated.

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[*] This paper, together with the analysis of the pressure distribution round the disk, to which reference is made herein (Proc. Roy. Soc. A, vol. cxxii. p. 604, 1929), was compiled in May 1926. Its publication has unfortunately been delayed, due to causes over which the author had no control. It was received by the Editor on March 18, 1929.

[†] Communicated by the Author.

5. Accession to Inertia due to Motion of Disk.
6. Simple Formulæ for Air-pressure and Power radiated.
7. Illustration of Analytical Expressions.
8. Current in Moving Coil.
9. Reactance of Moving Coil.
10. Axial Pressure.
11. Power radiated as Sound.
12. Transients.

ABSTRACT.

THE object of this paper is to examine analytically the performance of an arrangement akin to the type of loud speaker used for acoustic reproduction in which the driving agent is a circular coil situated in a strong radial magnetic field.

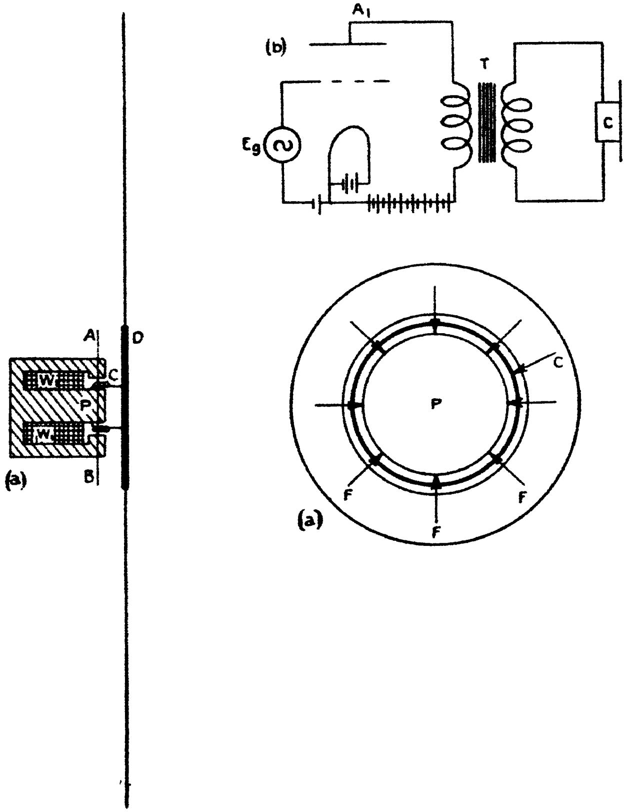
Accordingly the paper deals with the acoustic performance of a rigid disk, supported at its periphery and driven by a concentric circular coil situated in a radial magnetic field of constant value. Alternating current passed through the coil (which is connected in the anode circuit of a thermionic valve) causes the disk to vibrate axially. The simultaneous differential equations associated with the mechanical and electrical aspects of the problem are solved for the steady and the transient state, with and without elastic constraint at the periphery. Expressions are obtained for the acoustic radiation resistance, the acoustic power radiated, and the current in the moving coil. It is shown that the e.m.f. induced in the coil, due to its motion in the magnetic field, is concomitant with a capacity reactance in quadrature with the acoustic radiation resistance. By virtue of this and the inductance of the coil, the system has an electromechanical resonance frequency. If the damping is adequately small the mechanical system will execute oscillations in the absence of elastic constraint. Electrical circuit diagrams equivalent to the mechanical and electrical systems combined are given for the constrained and unconstrained conditions of the disk. These facilitate the study of transients.

The analysis is illustrated by curves showing the coil current, acoustic output, and axial pressure for three different disks. It is shown that, under set conditions, there is a certain size of disk for which the output is a maximum. A curve is also given by the aid of which the accession to inertia due to the divergence of the waves propagated by the disk can be evaluated.

(1) *Analysis of System without Elastic Constraint.*

THE essential components of the device to be analysed are shown in fig. 1. The diaphragm is situated in a plane wall of infinite extent so that there is no interference between the two sides. The disk is driven axially to and fro

Fig. 1.



(*a*) Illustrating arrangement of circular coil in radial magnetic field due to electromagnet.

On the right is an enlarged section at the plane AB. P = Central pin. C = Coil. D = Rigid disk. F = Radial magnetic field. W_1W_1 = Field winding.

(*b*) Showing valve-circuit connexions for supplying electrical energy to coil. A simplified equivalent circuit is given in fig. 2.

A_1 = Thermionic valve. E_g = sine-wave voltage to grid of valve (maximum). T = 1/1 transformer with zero leakage and self-capacity which gives the same alternating current performance as when the coil is connected in the valve circuit. C = Coil in magnetic field.

by means of a circular coil immersed in a strong radial magnetic field caused by a permanent magnet or an electromagnet. Alternating current of variable frequency is obtained in the anode circuit of the valve A_1 by applying a constant e.m.f. of sine-wave form to its grid and filament. Since the transformer T is assumed to be perfect, the alternating current passing through the primary is equal to that through the secondary. Moreover, so far as alternating current is concerned, the moving coil can be considered to be in the anode circuit of the valve. Thus the coil drives the disk, which consequently emits sound from both sides. In the analysis it will be assumed: (1) that the diaphragm is a perfectly rigid disk *; (2) that the restraint due to the suspension is negligible; (3) there is no loss due to eddy currents in the air; (4) the magnet etc. does not impede the sound-waves; (5) there is no mutual electromagnetic or electrostatic action between the moving coil and the magnet coil, or the permanent magnet, whichever is used; (6) there is no mutual acoustic action between the device and its surroundings, *i. e.*, it operates in undisturbed air.

The differential equations for the system are as follows:—

$$mD^2x + BDx = Ci, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$m\begin{cases} = \text{mass of disk and coil} + \text{equivalent mass of air on both sides of the disk.} \\ = M + M_1 = \text{effective mass of moving system.} \end{cases}$$

B = a factor depending on the alternating pressure due to sound-waves on both sides of the disk †.

$$C\begin{cases} = \text{force on moving coil per unit current (absolute).} \\ = \text{total flux interlinkages of field and coil.} \end{cases}$$

x = axial displacement of disk.

$$LDi + Ri + CDx = e, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

L = total inductance in coil circuit.

R = total resistance in coil circuit (including valve).

E = voltage applied to coil circuit (maximum value).

Instantaneous $e = E \sin(\omega t + \alpha)$.

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* Velocity of propagation of energy down disk is infinite, so that it moves as a whole at all frequencies.

† For analytical purposes this factor may be assumed to include additional linear damping, *e. g.*, fluid friction due to the viscosity of the medium. In the work herein the viscosity component has been omitted because its value is unknown.

Solving (1) and (2):

From (1) $$i=\frac{1}{C}(mD^2x+BDx).$$

Substituting for i in (2),

$$\frac{1}{C}(LD+R)(mD^2x+BDx)+CDx=e$$

or $$Dx=\frac{eC}{[mLD^2+(mR+BL)D+BR^2+C^2]}, \quad . \quad (3)$$

where $D=j\omega$ for a steady sine wave.

Substituting for D in (3):

Velocity of disk =

$$Dx=\frac{eC}{\{(BR+C^2-\omega^2mL)^2+\omega^2(mR+BL)^2\}^{\frac{1}{2}}}. \quad . \quad (4)$$

and the acoustic pressure on the disk at any instant $=BDx$.

The acoustic power factor may be defined as

Acoustic pressure/Driving force

or $$\cos\theta=\frac{B}{(B^2+\omega^2m^2)^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the load component BDx is in quadrature with the inertia component mD^2x.

Taking, now, the electrical side of the problem, we get from (1) and (2), solving for i,

$$Dx=\frac{1}{C}[e-i(R+LD)],$$

or $$D^2x=\frac{1}{C}[De+i(RD+LD^2)]. \quad . \quad . \quad . \quad (6)$$

Substituting from (6) in (1), we get

$$m[De-i(RD+LD^2)]+B[e-i(R+LD)]=C^2i;$$

$$\therefore \quad i\{C^2+BR+(BL+mR)D+mLD^2\}=mDe+Be$$
$$=e(mD+B). \quad . \quad (7)$$

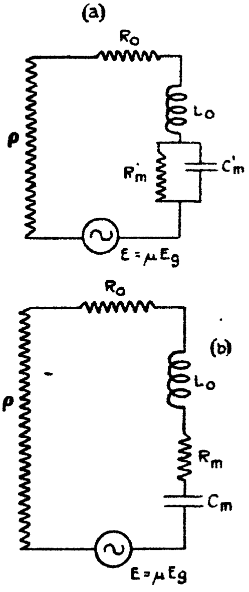
Substituting $D=j\omega$, we have

$$i=\frac{e(B^2+\omega^2m^2)^{\frac{1}{2}}}{\{(C^2+BR-\omega^2mL)^2+\omega^2(BL+mR)^2\}^{\frac{1}{2}}}. \quad . \quad (8)$$

The equivalent circuit for the coil is shown in fig. 2 (*a*). Here we have the internal alternating current valve resistance ρ in series with the alternating current resistance R_0 of the coil, when immovable; the inductance of the coil, when immovable, L_0; and a fictitious radiation resistance R_m' shunted by a fictitious motional condenser C_m'. For simplicity in manipulation the parallel circuit R_m', C_m' can be replaced by a series arrangement, as shown in fig. 2 (*b*). The values of R_m' and C_m' vary with the frequency, They are, of course, due to the back e.m.f. induced in the coil by the virtue of its motion in the magnetic field.

The power radiated as sound can be written $I^2_{\text{r.m.s.}} R_m$, where R_m is the effective motional or acoustic radiation resistance, as in fig. 2 (*b*).

Fig. 2.



μ = Amplification factor of valve.
E_g = Voltage change on grid of valve (maximum).
E = Fictitious alternator corresponding to voltage change on anode of valve.
ρ = Internal A.C. resistance of thermionic valve.
R_0 = Effective resistance ot coil when at rest.
L_0 = Effective inductance of coil when at rest.
$R_m' = C^2/B$ = Equivalent acoustic radiation resistance. } Parallel
$C_m' = m/C^2$ = Equivalent motional capacity. } arrangement.
R_m = Acoustic radiation resistance. } Series
C_m = Motional capacity. } arrangement.

Inserting the value of $I_{\text{r.m.s.}}$ from (8), we get

$$\text{Radiated power} = \frac{E^2_{\text{r.m.s.}}(B^2+\omega^2 m^2)R_m}{Q}, \quad . \quad . \quad . \quad (9)$$

where Q is the square of the denominator of (8).

Also

$$\begin{aligned} \text{Radiated power} &= \text{Pressure} \times \text{Velocity of disk}, \\ &= \mathrm{B}\dot{x}\dot{x} \text{ (the velocity being r.m.s. value)}, \\ &= \frac{\mathrm{BC}^2\mathrm{E}^2_{\text{r.m.s.}}}{\mathrm{Q}} \text{ from (4)}. \quad \ldots\ldots \quad (10) \end{aligned}$$

Equating (9) and (10), we get

$$\begin{aligned} \mathrm{R}_m &= \frac{\mathrm{BC}^2}{(\mathrm{B}^2+\omega^2 m^2)} \\ &= \frac{\mathrm{C}^2\cos^2\theta}{\mathrm{B}} \text{ from (7)}. \quad \ldots \quad (11) \end{aligned}$$

The two components of the back e.m.f. due to the motion of the coil are in quadrature. Moreover, it can be shown that

$$\begin{aligned} \tan\theta &= \text{reactance/resistance} \\ &= \frac{1}{\omega \mathrm{C}_m \mathrm{R}_m} \end{aligned}$$

or

$$\mathrm{C}_m = \frac{1}{\omega \mathrm{R}_m \tan\theta}.$$

Substituting the value of R_m from (11), we get

$$\mathrm{C}_m = \frac{m}{\mathrm{C}^2\sin^2\theta} = \frac{m}{\mathrm{C}^2(1-\cos^2\theta)}. \quad \ldots \quad (12)$$

Now, the current in the moving coil is (see fig. 2 (*b*))

$$\frac{\text{Voltage}}{\text{Impedance}} = \frac{\mathrm{E}}{\mathrm{Z}}$$

or

$$\mathrm{I} = \frac{\mathrm{E}}{\left[(\mathrm{R}+\mathrm{R}_m)^2 + \left(\omega\mathrm{L} - \frac{1}{\omega\mathrm{C}_m}\right)^2\right]^{\frac{1}{2}}}. \quad \ldots \quad (13)$$

The acoustic pressure = Force due to current in coil × Acoustic power factor = $\mathrm{CI}\cos\theta$

$$= \frac{\mathrm{EC}\cos\theta}{\mathrm{Z}}. \quad \ldots\ldots\ldots \quad (14)$$

It can be shown that when the condenser and resistance are in parallel

$$\mathrm{R}_m{}' = \frac{\mathrm{C}^2}{\mathrm{B}} \quad \text{and} \quad \mathrm{C}_m{}' = \frac{m}{\mathrm{C}^2}.$$

Thus, as *f* increases, both $\mathrm{R}_m{}'$ and $\mathrm{C}_m{}'$ decrease. These formulæ comply with equation (6), and are therefore valid for the transient and for the steady state. By means of fig. 2 *a* it is possible to study the effect of transients. If we imagine a battery to be suddenly switched in to replace the alternator in fig. 1, a voltage will be applied to the circuit rising from zero to E instantaneously. This can be resolved into an infinite spectrum of frequencies. The low frequencies will be impeded by C_m', although part will be by-passed by R_m'. The high frequencies will be by-passed by C_m' but impeded by L_0. Thus there will be a definite phase-shift of the high- and low-frequency components of the impulse. The attenuation of the former by L_0 will reduce the rate of rise of the current so that the impulse profile will be rounded. Hence, to reduce distortion with transients of steep wave front, *e.g.*, piano, gun-firing, the coil inductance should be small. There is also the transient when the battery is replaced by a short-circuit. In the ideal case the current in the system would cease immediately. But the electromagnetic energy $\frac{1}{2}Li^2$ and the electrostatic energy $\frac{1}{2}C_m'v^2$ have to be dissipated. Since this occupies a definite time-interval, there is a rounding of the transient. From a physical standpoint the charge to C_m' is represented by the mechanical moving system gradually increasing in velocity. The by-passing effect of R_m' is the damping effect of the air on the moving disk. As the velocity increases, so also does the back e.m.f., thereby reducing the coil current. The charging current of C_m' falls exponentially.

When the battery is replaced by a short-circuit, the kinetic energy of the mechanical system is expended in keeping the disk in motion against the air and the electromagnetic damping. This is represented by the discharge of C_m' through R_m' and the remainder of the circuit. The disk comes to rest exponentially.

Coming to the steady state, this is more readily seen by the aid of fig. 2 (*b*). The condenser C_m means increased impedance at low frequencies. There is electromechanical resonance in the middle register, the current being a maximum and falling away on either side. Hence the force acting on the coil varies with the frequency. To reduce the variation in impedance it is essential to use a power valve whose internal resistance is large compared with the capacitive and inductive reactances.

(2) *Andlysis of System with Elastic Constraint.*

This case includes not only a coil drive in which the rigid disk is supported elastically at the periphery, but also a rigid disk freely supported at the periphery and driven by an electromagnetically operated reed or other elastic member at the centre.

The equations are now

$$mD^2x + BDx + k_1x = Ci, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$LDi + Ri + CDx = e, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which, on solution for the steady state, yield

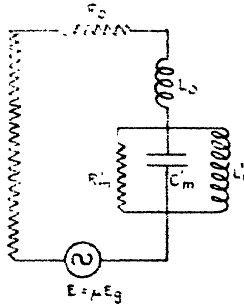
$$Dx = \frac{e\omega C}{\{[\omega^2(k_1L + BR + C^2) - \omega^2 mL]^2 + [k_1R - \omega^2(BL + Rm)]^2\}^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (17)$$

and

$$i = \frac{e[(k_1 - \omega^2 m)^2 + \omega^2 B^2]^{\frac{1}{2}}}{Q_1}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where Q_1 is the denominator of (17) and k_1 the coefficient of restitution.

Fig. 3.



$R_m' = C^2/B$. $L_m' = C^2/k_1$.
$C_m' = m/C^2$. k_1 = coefficient of restitution.

See fig. 2 for meaning of other symbols.

The equivalent electrical circuit for this case is shown in fig. 3. Here we have a circuit identical with that for the coil drive without constraint, except that now there is an inductance $L_m' = C^2/k_1$ in parallel with R_m' and C_m', which have the same values as before. Here we have two possibilities of resonance, viz., L_0 with C_m' and L_m' with C_m'. The resonances are modified, of course, by R_m'. The first, which corresponds to the electromechanical resonance, is still further modified by L_m', and the second, which corresponds to the resonance of the elastic constraint, is modified by L_0.

The problem of transients in this case can be analysed in the same manner as that indicated in connexion with fig. 2 (*b*). For both figs. 2 (*b*) and 3 the damping for the $L_0\, C_m'$ combination is such that oscillation does not occur, but for the $L_m'\, C_m'$ case, unless P, R_0 and R_m' are sufficiently small, an impulse will call forth the natural note of the system. This latter condition must be avoided in practical work.

(3) *Transient Solution.*

For the transient solution of the problem, we shall neglect the damping due to acoustic radiation, since it is small compared with that due to the motion of the coil in the magnetic field. We shall consider the question of the decay of the oscillations when the operating current in the coil ceases. So far as the time constant of the coil at rest is concerned, this is usually quite low enough to be neglected by comparison. It is generally less than 10^{-4} second.

The equations are now

$$mD^2x = Ci. \quad \ldots \ldots \quad (19)$$

$$LDi + Ri + CDx = 0. \quad \ldots \ldots \quad (20)$$

Hence, substituting from (19) in (20),

$$\left[D^3 + \frac{R}{L}D^2 + \frac{C^2}{mL}\right]x = 0\,; \quad \ldots \ldots \quad (21)$$

$$\therefore \quad Dx = 0, \quad i.e., \quad x = X_1 \text{ a constant} \quad . \quad (22)$$

and

$$\left(D^2 + \frac{R}{L}D + \frac{C^2}{mL}\right)x = 0. \quad \ldots \ldots \quad (23)$$

There are the usual three solutions for the aperiodic, critical, and oscillatory cases of (21).

Aperiodic.

$$x = Ae^{\lambda_1 t} + Be^{\lambda_2 t} + X_1, \quad \ldots \ldots \quad (24)$$

where

$$\left.\begin{matrix}\lambda_1\\ \lambda_2\end{matrix}\right\} = -\frac{R}{2L} \pm \left[\frac{R^2}{4L^2} - \frac{C^2}{mL}\right]^{\frac{1}{2}} \quad \text{and} \quad \frac{C^2}{mL} < \frac{R^2}{4L^2}.$$

Critical.

$$x = e^{-\frac{Rt}{2L}}(At + B) + X_1, \quad \ldots \ldots \quad (25)$$

where

$$\frac{C^2}{mL} = \frac{R^2}{4L^2}.$$

Oscillatory.

$$z = e^{-\frac{Rt}{2L}}(A\cos\beta t + B\sin\beta t) + X_1, \quad . \quad . \quad (26)$$

where

$$\beta = \left[\frac{C^2}{mL} - \frac{R^2}{4L^2}\right]^{\frac{1}{2}} \quad \text{and} \quad \frac{C^2}{mL} > \frac{R^2}{4L^2}.$$

In practice, where a conical diaphragm would be used in place of the rigid disk, the motion is usually aperiodic. The oscillatory case, however, is of interest, for it shows that oscillations can occur without mechanical constraint. The explanation is simply that the kinetic energy $\frac{1}{2}mv^2$ is stored and re-stored as electrokinetic energy $\frac{1}{2}Li^2$, *i. e.*, the coil is brought to rest by generating an opposing current due to its cutting the magnetic field. This current then sets the disk and coil in motion in the opposite direction, the damping being the same as that of the coil at rest, since we agreed to neglect the motional resistance. It is obvious that this condition must be avoided in practice, or every transient would start and stop to the accompaniment of the natural electromechanical frequency.

Solving the aperiodic case, we get the linear velocity

$$Dx = \frac{v}{\lambda_1 - \lambda_2}\{\lambda_1 e^{\lambda_2 t} - \lambda_2 e^{\lambda_1 t}\}, \quad . \quad . \quad . \quad (27)$$

where v is the velocity of the disk when the driving force ceases.

The time taken to come to rest under the usual hypothesis is infinite. However, in our case it is only necessary to find the time taken for the velocity to be reduced to a certain percentage of its maximum value, *e.g.*, 10 per cent.

So far as the critical case is concerned, the linear velocity is

$$Dx = ve^{-\frac{Rt}{2L}}\left(\frac{Rt}{2L} + 1\right). \quad . \quad . \quad . \quad . \quad (28)$$

In the oscillatory case we have the natural frequency, as

$$f = \frac{1}{2\pi}\left[\frac{C^2}{mL} - \frac{R^2}{4L^2}\right]^{\frac{1}{2}} = \frac{1}{2\pi}\left[\frac{1}{LC_m} - \frac{R^2}{4L^2}\right], \quad . \quad (29)$$

and the linear velocity is

$$Dx\, ve^{-\frac{Rt}{2L}}\left\{\cos\beta t - \frac{\alpha}{\beta}\sin\beta t\right\}. \quad . \quad . \quad . \quad (30)$$

(4) *Acoustic Pressure on Disk and Power radiated.*

The pressure on a rigid circular disk vibrating in an equal circular aperture situated in a rigid plane plate of infinite extent has been treated analytically by the late Lord Rayleigh[*]. He assumed that there was neither eddy current nor other source of loss, and that the amplitude of motion of the disk on its axis is insufficient to affect appreciably the wave progagation in the neighbourhood of the disk. The total pressure on the disk is the vector sum of two components in quadrature: (*a*) the acoustic pressure in phase with the velocity, (*b*) an inertia component 90° out of phase with the velocity which arises due to divergence of waves from the disk. The latter is in effect a mass to be added to the disk, and is treated in the next section. The result given by Rayleigh is as follows:—

Acoustic pressure due to radiation of sound-waves from *both* sides of the disk is $P_{\text{r.m.s.}}$

$$\left\{ \begin{aligned} &= 2\rho_d A c\left[1-\frac{J_1(2ka)}{ka}\right]\dot{X}, \\ &= B\dot{X}, \quad . \quad . \quad . \quad . \end{aligned} \right. \qquad (31)$$

where

$$B = 2\rho_d A c G \text{ and } G = \left[1-\frac{J_1(2ka)}{ka}\right].$$

ρ_d = density of air (in gms. per cm.^{3}).

A = area of disk (in cm.^{2}).

c = velocity of sound (cm. per sec.).

$k = \omega/c$.

a = radius of disk (in cm.).

$\dot{X}$ = r.m.s. axial velocity of disk (cm. per sec.).

$y = x \tan \omega t$ (instantaneous value).

The power radiated is

$$\begin{aligned} W &= \text{pressure} \times \text{axial velocity (r.m.s. values)}, \\ &= B\dot{X}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned} \qquad (32)$$

For a simple harmonic motion apart from phase. } $\dot{X} = \omega Y$, where Y is an r.m.s. value.

Thus

$$P_{\text{r.m.s.}} = B\omega Y \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

and

$$W = B\omega^2 Y^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

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[*] 'Sound,' ii. p. 162.

Now,

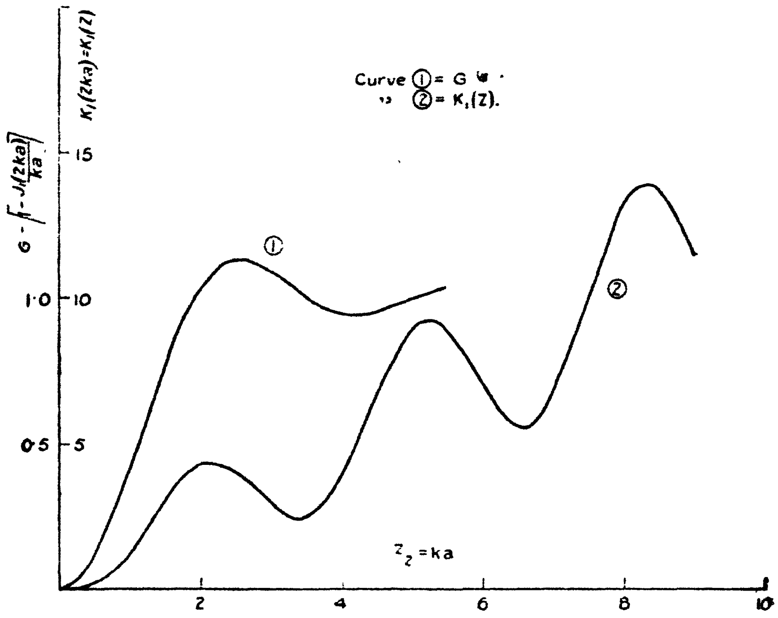
$$G=\left[1-\frac{J_1(2ka)}{ka}\right]=\frac{k^2a^2}{1.2}-\frac{k^4a^4}{1.2^2.3}+\frac{k^6a^6}{1.2^2.3^2.4}\text{ etc.},$$

so that when ka is small, G is approximately equal to

$$\frac{k^2a^2}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (35)$$

As ka increases, G gradually increases due to decrease in the term $\frac{J_1(2ka)}{ka}$. When $ka=1{\cdot}9$, G becomes unity, and

Fig. 4.



Curves illustrating the functions G and K_1 (z).

as ka is increased, G ultimately oscillates about this value, as shown in fig. 4. Interpreted in the physical sense, when the frequency or the diaphragm is large enough to violate the relationship $G=k^2a^2/2$ appreciably, interference of the radiation from various parts of the disk occurs in space, *i. e.*, there is a transition from spherical wave propagation. As the frequency or the diameter is still further increased, the focussing of the sound due to interference gradually becomes more pronounced until $G=1$, after which the interference causes the pressure on the disk to oscillate from lower to higher values, *i.e.*, the wave propagation is sensibly plane. Up to the point $ka=0{\cdot}3$, the value of G is substantially $k^2a^2/2$, whilst for $ka=0{\cdot}5$ the error is only +5 per cent., which is small so far as aural appreciation is concerned. Thus, for a disk 10 cm. radius, focussing in air at N.T.P. would begin when $f=250 \sim$. For a disk 5 cm. radius the frequency would be $500 \sim$, *i.e.*, the frequency at which focussing begins is inversely proportional to the diameter of the disk. Since focussing depends upon the velocity of propagation of sound, it is clear that it will commence at a higher frequency in a gas whose density at N.T.P. is less than that of air. For example, in hydrogen the density is about 1/16 (actually 1/14·3) that of air, thereby giving a fourfold increase in velocity. Thus focussing would commence at frequencies four times those cited above.

As another instance we may take the case of water, where the velocity of propagation of pressure waves is approximately four times that in air. Here also the focussing would commence at frequencies four times those cited above.

The effect of focussing is to reduce the acoustic pressure on the disk, and, depending upon the mechanism driving the disk, the power radiated as sound is modified accordingly. For instance, with a coil-driven disk 10 cm. radius the power decreases to a very low value at high frequencies. In the upper audio-frequency register the amplitude of motion $X \propto 1/f^2$. If the amplitude varied so that $B\omega^2X^2$ (or $B\omega^2Y^2$) were constant, the power would be constant, but the axial pressure would increase with the frequency.

When G becomes oscillatory, the value is approximately unity, so that the pressure on the disk is $P_{r.m.s.}=2\rho_d Ac\omega Y$ and the power radiated $2\rho_d Ac\omega^2Y^2$. At the higher frequencies $Y \propto 1/f^2$, and it follows that the pressure falls off as $1/f$ and the power as $1/f^2$, provided, of course, the current in the coil is constant.

(5) *Accession to Inertia due to Motion of Disk.*

In addition to the acoustic pressure or useful work component, there is a second component of the total pressure on the disk. This component is in quadrature with the acoustic pressure, and can be regarded as an accession to inertia which is to be added to the mass of the disk *. According to Rayleigh, the accession to inertia—which is due to the waves diverging from the source—for both sides of the disk is given by the expression :

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* 'Sound,' *loc. cit.* At frequencies where the wave propagation is sensibly plane the accession to inertia is evanescent.

$$M_1 = \frac{\rho_d \pi K_1(2ka)}{k^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Putting $2ka = z$, we have

$$K_1(z) = \frac{2}{\pi}\left[\frac{z^3}{1^2 . 3} - \frac{z^5}{1^2 . 3^2 . 5} + \frac{z^7}{1^2 . 3^2 . 5^2 . 7}\right] - \text{etc.,} \quad (37)$$

or

$$\frac{\rho_d \pi K_1(z)}{k^3} = \frac{16a^3\rho_d}{3} = \frac{16a}{3\pi} \cdot \pi a^2 \rho_d, \quad . \quad . \quad . \quad (38)$$

which means that the inertia component is equivalent to a cylinder of air whose radius is that of the disk and whose height is $16a/3\pi$. The error involved in this assumption is about 5 per cent. when $ka = 0{\cdot}43$ and increases for higher values of ka. As ka increases, the value of M_1 decreases, *i.e.*, the accession to inertia is reduced. For a disk of given size the inertia effect falls off as the frequency rises above the value which satisfies the relation $ka = 0{\cdot}43$. Thus, for a disk 10 cm. radius at 50 ~ $M_1 = 7{\cdot}0$ gm., whereas at 1000 ~ it is only 2·4 gm. For a small disk say, 2 cm. radius, the value of M_1 is almost constant up to 1000 ~. Moreover, although the value of M_1 increases with the size of the disk, the frequency range—from zero upwards—over which it remains sensibly constant decreases. Thus, with a large diaphragm driven by an alternating force of *constant magnitude* the radiation in the bass register will be defective due to inertia effect.

The decay in inertia effect is due to interference, since the solid angle over which the radiation extends gradually diminishes, *i. e.*, the divergence decreases as the frequency increases. Furthermore, the energy distribution within the angular space is not uniform, but tapers away from the axis outwards.

The function $K_1(2ka)$ is plotted in fig. 4 partly from equation (37). Rayleigh gives an alternative series for this function, which is more amenable—and was therefore used—to the computation of $K_1(z)$ for large values of the argument than that of equation (37). It is of interest to mention that when z is very great $K_1(z)$ tends to the value $2z/\pi$, which is also very great.

(6) *Simple Formulæ for Air-pressure and Power radiated.*

From sections 4 and 5 we can deduce simple formulæ which are applicable under certain conditions at high and low frequencies.

At low frequencies, when $ka < 0{\cdot}4$ the value of G is

$$\frac{k^2a^2}{2} \quad \text{and} \quad M_1 = \frac{16}{3}a^2\rho_d,$$

which is constant. Thus

$$\begin{aligned} B &= \rho_d A c k^2 a^2 \\ &= \frac{\rho_d A^2 \omega^2}{\pi c}, \qquad \ldots\ldots \qquad (39) \end{aligned}$$

since $A = \pi a^2$.

Also r.m.s. force = mass × r.m.s. acceleration.

$$\begin{aligned} F &= m\omega^2 X \\ &= m\omega^2 Y, \end{aligned}$$

where F, X, and Y are r.m.s. values for a sine-wave motion (phase not in question).

But the pressure on the disk

$$\begin{aligned} &= B\omega Y \\ &= \frac{\rho_d A^2}{\pi c}\left(\frac{F}{m}\right).\omega. \qquad \ldots\ldots \qquad (40) \end{aligned}$$

Thus the pressure on the disk increases directly with the frequency.

$$\begin{aligned} \text{Power radiated} &= B\omega^2 Y^2 \\ &= \frac{\rho_d A^2}{\pi c}.\frac{F}{m} = \text{a constant}. \qquad \ldots\ldots \qquad (41) \end{aligned}$$

Moreover, the power radiated at low frequencies is constant, *provided* F *is constant, i. e.*, when the coil current is constant, in spite of the fact that the total pressure on the disk decreases in proportion to the frequency. This apparent paradox is explained when we realize that the amplitude of vibration increases inversely as the square of the frequency.

At high frequencies where $ka > 1{\cdot}9$ the wave propagation is sensibly plane and the value of G oscillates about unity. Taking its value as unity, *i.e.*, neglecting the oscillation of G, we have

$$B = 2\rho_d A c = \text{a constant}$$

and

$$B\omega Y = 2\rho_d A c.\frac{F}{m}.\frac{1}{\omega}, \qquad \ldots\ldots \qquad (42)$$

so that the pressure on the disk now varies *inversely* as the frequency (compare with equation (40)).

$$\text{Power radiated} = B\omega^2 Y^2$$

$$= 2\rho_a A c \left(\frac{F}{m}\right)^2 \cdot \frac{1}{\omega^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (43)$$

Thus the power radiated at high frequencies varies inversely as the square of the frequency, provided the coil current is constant.

(7) *Illustration of Analytical Expressions.*

The ultimate performance of the device under consideration depends, amongst other things, upon the current in the moving coil. To determine this, it is imperative to know m, $\cos\theta$, C_m, and R_m. These factors have been calculated for three disks of different sizes, namely, 5 cm., 10 cm., and 15 cm. radius respectively. Moreover, the influence of the size of the disk can be seen. The results have been tabulated and are given in Tables I., II., and III. The effective mass is the sum of that due to disk, coil (5 gm.) and accession to inertia.

TABLE I.

Radius of disk = 5 cm. Mass of disk = 2·5 gm.

f. Frequency (cycles per second).	m. Effective mass (gm.).	Cos θ. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50 ……	8·36	$2{\cdot}8\times10^{-3}$	0·33	26	0·52
100 ……	8·36	5·7	0·33	26	0·52
200 ……	8·36	11·4	0·33	26	0·52
500 ……	8·3	28·5	0·33	26	0·5
1000 ……	8·16	52	0·33	25	0·46
2000 ……	7·82	69	0·31	17·5	0·3
4000 ……	7·53	36	0·3	4·8	0·08
8000 ……	7·5	18	0·3	1·2	0·018

The variation in effective mass is more pronounced the greater the diameter of the disk. In each case the mass decreases with rise in frequency, which can be attributed to reduction in the accession to inertia caused by the interference effect described in a former paper*. The acoustic power factor, and therefore the total sound-pressure on the disk, increases with the diameter *. In each of the three cases the power factor attains a maximum value. This is

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* McLachlan, Proc. Roy. Soc. A, vol. cxxii. p. 604 (1929).

TABLE II.

Radius of disk = 10 cm. Mass of disk = 10 gm.

f. Frequency (cycles per second).	m. Effective mass (gm.).	Cos θ. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50	22	$1{\cdot}8\times10^{-2}$	0·88	66	1·3
100	22	3·6	0·88	66	1·3
200	22	7·2	0·88	66	1·3
500	20·2	17	0·81	69	1·3
1000	17·4	25	0·7	58	1·07
2000	15·2	14	0·61	18	0·31
4000	15	7	0·6	4·5	0·07
8000	15	3·5	0·6	1·1	0·015

TABLE III.

Radius of disk = 15 cm. Mass of disk = 22·5 gm.

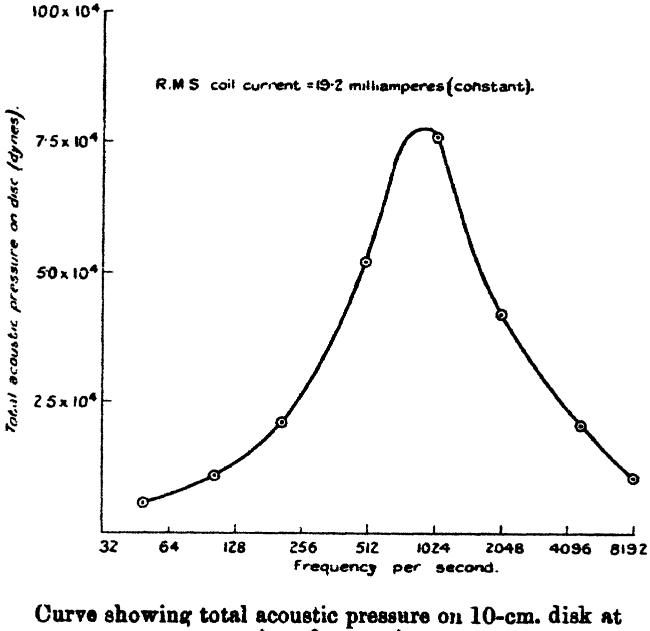
f. Frequency (cycles per second).	m. Effective mass (gm.)	Cos θ. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50	50·7	$3{\cdot}77\times10^{-2}$	2·0	59	1·18
100	50·7	7·2	2·0	57	1·17
200	49·5	14·5	2·0	58	1·15
500	40·4	32	1·66	59	1·13
1000	29·3	35	1·14	46	0·85
2000	27·5	17·1	1·1	12	0·21
4000	27·5	8·7	1·1	1·3	0·02
8000	27·5	4·4	1·1	0·3	0·005

explained by a consideration of the velocity of the disk and the interference at various frequencies.

* The variation in the total pressure (inertia and acoustic components) has been treated by A. G. Warren, Proc. Phys. Soc.

Assuming the axial driving force and the effective mass to be constant, the power radiated is also constant. The acoustic pressure is power/velocity; and since velocity $\propto 1/f$, the pressure increases with frequency, provided the wave propagation is spherical, *i. e.*, the waves are divergent about the source. But a point is reached when the propagation deviates from the spherical variety and gradually assumes the nature of plane waves. Moreover, as the frequency increases from 50 cycles upwards, a turning-point is reached due to interference, where the total pressure on the disk decreases. A curve illustrating this effect is given in fig. 5, whilst the analytical aspect of the problem is obvious from expressions 39, 40, 42.

Fig. 5.



Curve showing total acoustic pressure on 10-cm. disk at various frequencies.

The motional capacity which exists by virtue of the back e.m.f. induced in the coil due to its motion in the magnetic field, increases with the mass (and radius) of the disk. This is explained by the reduced axial motion and therefore lower velocity of the larger disk, which generates a smaller back e.m.f. In each case the motional capacity decreases with rise in frequency, owing to the reduction in the accession to inertia of the disk.

So long as the wave propagation is spherical, the acoustic radiation resistance R_m is substantially constant. When, however, interference commences, R_m decreases until at 8000 ~ it is a small fraction of its value at 50 ~. From the tabular values it is seen that over the range 50 to 2000 cycles the greatest output is obtained from a disk 10 cm. radius. Above 2000 cycles the output is greatest from the smallest disk, viz., 5 cm. radius. If the mass of a disk driven by a constant axial force varies as the square of the radius, the radiation over a given band of frequencies increases with decrease in the size of the disk. At the higher frequencies this must be clear, since the interference effect is less prominent with small disks than with large ones, whilst at low frequencies the accession to inertia is less. Now, this is not in keeping with the results just quoted. The apparent paradox can readily be explained if we consider the effect of the coil. Its mass is a much greater proportion of the total mass with a small than with a large diaphragm. Hence the acoustic power factor and the output of the small diaphragm are reduced accordingly. Moreover, in the present system there is a certain radius of disk for which the acoustic output over a definite frequency band is a maximum.

The combined efficiency of the arrangement is given by the ratio *

$$R_m/(R_m+R_0+\rho), \quad \text{where} \quad (R_m+R_0+\rho)$$

is the total A.C. resistance of the circuit of fig. 2, including the valve. Owing to the lack of "coupling" between the disk and the transmission medium (air), and to the large values of R_0 and ρ, the efficiency is very low. When disks of 2·5 cm. radius are used, the "coupling" can be increased very materially by using a suitable horn, and an overall efficiency (including valve) of from 7 to 10 times the cited figures is obtained. In practice, however, to secure ample output in the low frequency register, the length of the horn has to exceed 10 feet, which is not always convenient.

(8) *Current in the Moving Coil.*

The coil current at any frequency is controlled by the impedance of the coil in motion, together with ρ, the internal alternating current resistance of the valve. The latter has been allotted an average value of 4000 ohms. The motional-coil impedance depends upon four factors, namely: (1) the effective resistance at rest, (2) the acoustic radiation resistance, (3) the effective inductance at rest, (4) the motional capacity. Items (1) and (3) have been ascertained by bridge measurements, whilst (2) and (4) have been calculated from the formulæ developed herein.

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* The inherent efficiency is $\frac{R_m}{R_m+R_0}$ and is several times that of the overall efficiency, since the latter is reduced considerably by the valve.

TABLE IV.

Effective Inductance and Resistance of 1000-turn coil fixed in electromagnet.

f. Frequency (cycles per sec.).	L_0. Effective inductance coil at rest (henry).	R_0. Effective resistance coil at rest (ohms).
50	0·27	960
100	0·26	1000
200	0·24	1050
500	0·2	1170
1000	0·15	1360
2000	0·13	1760
4000	0·12	2250
8000	0·11	2750

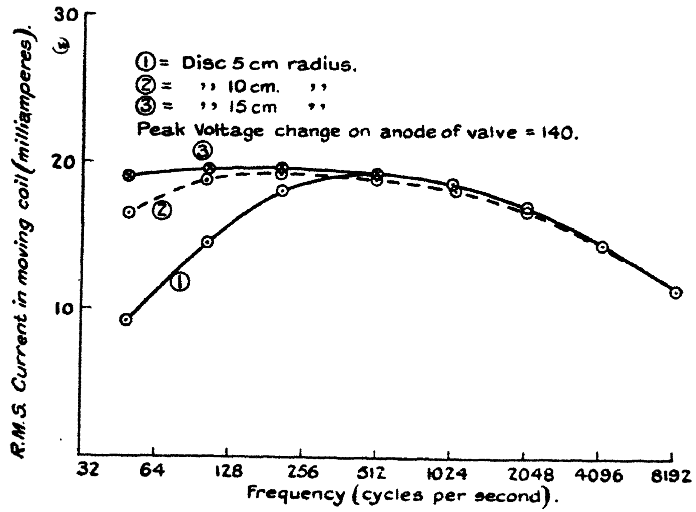
Details of Coil and Magnetic Field.

Mean radius of coil	$r=2{\cdot}5$ cm.
Number of turns of 46 enamelled wire.	$n=10^3$.
Mass of coil	$=5$ gm.
Mean strength of radial magnetic field.	$H=10^4$ c.g.s. units.
Coil constant	$C=\begin{cases}2\pi rnH.\\ 1{\cdot}58\times10^8.\end{cases}$
Internal resistance of valve	$\rho=4\times10^3$ ohms.

The values of effective inductance and resistance of the coil when firmly fixed in the electromagnet with the field on are given in Table IV. Due to eddy currents in the iron the inductance decreases, whilst due to eddy current and hysteresis losses the resistance increases with rise in frequency. The former is useful, since it entails reduced inductive reactance and greater current at the upper frequencies. At these frequencies a movement of the order of 10^{-6} cm. produces quite an appreciable sound, and it is difficult to fix the coil to prevent this occurring. However, as R_m is relatively small and C_m of negligible importance, any errors in measurement involved due to minute motion of the coil are immaterial. In fact, throughout the entire acoustic range, only a small error is involved if the inductance and resistance are determined with the magnet winding short-circuited upon itself, there being no radial field.

Using expression (13) and postulating a peak sine-wave voltage change of 140 volts on the anode of the valve, the coil current has been calculated for three disks at frequencies varying from 50 to 8000 cycles per second. The results are shown pictorially in fig. 6. At low frequencies the larger the diaphragm the larger the current. This is due to the lesser amplitude and velocity of the larger disk by virtue of its greater inertia. Thus the back e.m.f. induced by the motion of the coil in the magnetic field decreases as the radius of the disk increases. At the higher frequencies, although the induced e.m.f. is negligible, the coil current is curbed due to increase in the effective resistance (iron loss) and reactance of the coil. Moreover, the coil current at these frequencies is approximately the same for all three disks.

Fig. 6.

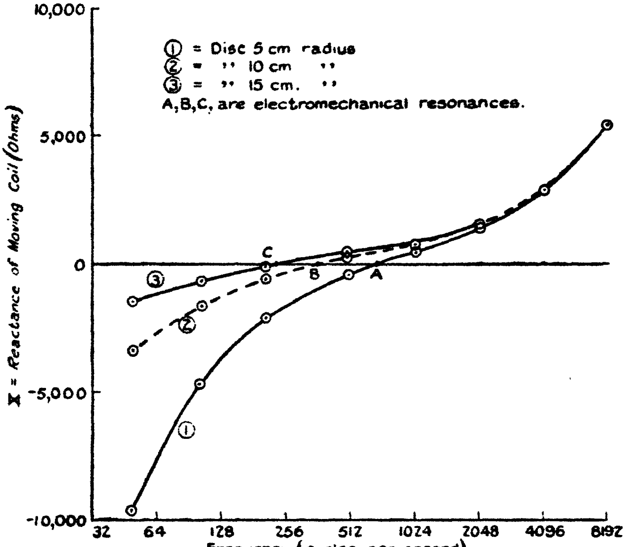


Curves showing current in moving coil at various frequencies.

(9) *Reactance of Moving Coil.*

The reactance of the coil, namely $\left(w\mathrm{L}_0-\frac{1}{w\mathrm{C}_m}\right)$, varies from a negative value through zero to a positive value, the latter being due to its inductance. The negative reactance at low frequencies exists by virtue of the large back e.m.f. induced in the moving coil, *i. e.*, the motional capacity. Since the smaller the disk the larger the amplitude, and therefore the axial velocity, the low-frequency reactance of the 5-cm. disk is greater than that of the other two. When the reactance is zero, $w\mathrm{L}_0=\frac{1}{w\mathrm{C}_m}$, and this occurs at the electromechanical resonance frequency. The greater the effective mass of the disk and coil the lower the electromechanical resonance frequency. These points are depicted diagrammatically by the reactance curves of fig. 7. At frequencies above and below the resonance point, the current "lags" and "leads" respectively the impressed e.m.f. $\mathrm{E}=\mu\mathrm{E}_g$ of fig. 2. The further the frequency from

Fig. 7.



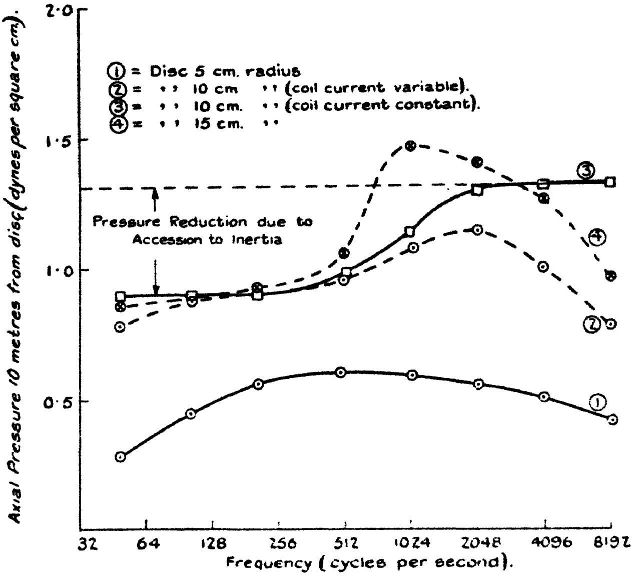
Curves showing "reactance" of moving coil at various frequencies.

resonance the greater the "wattless" component of the current.

(10) *Axial Pressure.*

It has been shown * that the axial pressure at distances exceeding a certain number of diameters from the disk is independent of the frequency, so long as the acceleration of the disk is constant and *f* is not too high. This necessitates constant driving force and effective mass throughout the frequency range under consideration. In our particular case both of these factors are variable. The deviation from constant pressure is seen from the curves of fig. 8. Curves 1, 2, and 4 indicate the pressure variation for the three disks when the current † and effective mass vary with the frequency. The pressure caused by the 5-cm. disk is relatively small, due to the influence of the mass of the coil, as explained previously. At the lower frequencies, there is little difference between

Fig. 8.



Curves showing axial pressure 10 metres from disk at various frequencies.

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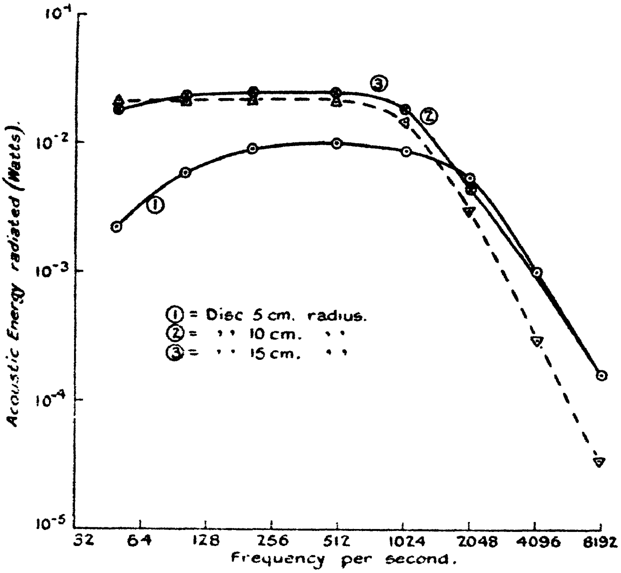
* Proc. Roy. Soc. *loc. cit.*

† See fig. 6.

the pressures caused by the 10-cm. and 15-cm. disks, but the pressure is greater for the 15-cm. disk at the higher frequencies, although the total energy output is less due to enhanced interference.

Curve (3) indicates the pressure variation for the 10 cm. disk when the driving force is constant. The smaller pressure at frequencies below 2000 cycles is due to the greater effective mass caused by "accession to inertia." In each case the oscillations in the curves at the higher frequencies concomitant with oscillation in the function G have been disregarded.

Fig. 9.



Curves illustrating power radiated at various frequencies.

(11) *Power radiated as Sound.*

The power radiated as sound from the three disks is portrayed graphically in fig. 9. The vertical scale is a logarithmic one, since the sensitivity of the ear progresses in a logarithmic manner. The output from the two larger disks is appreciably greater than that from the 5-cm. disk over the frequency range 50 to 1000 cycles. Thereafter the output from the larger disks falls off rapidly, until at the higher frequencies it is very small for all three disks.

This is, of course, due to interference concomitant with plane-wave propagation.

(12) *Transients.*

The preceding curves all relate to the steady state, and it remains, therefore, to indicate what results are to be expected when the e.m.f. applied to the grid of valve A_1 (fig. 1) is of a transient nature. The transformer is assumed not to affect the transient in any manner.

Taking the simplest case first, suppose the coil current is a replica in magnitude and time-displacement of the e.m.f. representing the transient as applied to the grid of the valve. Further, let us assume the disk to be so small that the accession to inertia is either constant or negligible over the important frequency range embodied by the transient. The force on the disk, and therefore its acceleration, is then a replica of the e.m.f. applied to the grid. But we have already shown * that the axial pressure at a point several diameters from the disk varies directly as the acceleration of the disk. Hence, under these conditions the acoustic reproduction of the transient at a point on the axis will be perfect, provided the pressure variations at the said point are in phase with the aeceleration of the disk.

This is substantially correct when the frequency is small compared with the product of sound velocity and axial distance. If this condition is violated, there will be a phase-shift of the higher frequency components of the impulse, thereby altering its shape and causing distortion. Moreover, the higher the component frequencies of the transient the greater must be the distance from the disk to obtain distortionless reproduction.

With any of the three disks treated above, the effective mass varies with the frequency, and under a condition where grid e.m.f. and coil current were related linearly there would be a relatively reduced acceleration corresponding to the low-frequency components of the impulse. Thus the axial pressure of these components would be reduced relative to the high-frequency components, thereby causing distortion.

In the practical case, the coil current for a given e.m.f. applied to the valve grid depends upon the impedance of the complete anode circuit of the valve (see fig. 2 (*a*)). The current, as we see from fig. 6, varies appreciably with the frequency, there being a maximum value at the electro-mechanical resonance point. On either side of this frequency the component sine-wave oscillations, into which the impulse can be analysed, are reduced in magnitude and altered in phase. Moreover, distortion occurs throughout the frequency range. By keeping the time-constant of the circuit as small as possible—3×10^{-5} is a practical figure,—the distortion of the components at the upper end of the frequency range can be reduced.

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* Proc. Roy. Soc. *loc. cit.*

By combining the effect of variation in the effective mass of the disk with that due to variation in impedance, we obtain the resulting distortion of the transient. The effective mass of the disk and the driving force for a given e.m.f. both vary with frequency, so that the acceleration, and therefore the axial pressure, follow suit. The precise degree of distortion depends, of course, upon the shape of the transient, *i.e.*, upon the relative magnitudes and phases of its components.

Hitherto we have only dealt with the question of transients as registered by pressure variations on the *axis* of the disk. If we choose a point at an angular distance from the axis, we are faced with the evanescence of the higher frequencies due to interference. Moreover, to the preceding causes of distortion associated with transients the influence of focussing at the higher frequencies must be added.

It has been shown experimentally that in *the steady state* the ear is indifferent to the phases of the various component frequencies of a sound. From experimental observation the author is inclined to the view that this is inapplicable to transients. In the latter case it is probably the shape of the wave-front which counts, *e.g.*, gun-firing, piano, hand-clapping. The rapidity of response of the ear to sounds of varying suddenness has not been measured *, so that it is impossible to make any definite statement of the subject. It seems rational, however, that a degree of wave-front steepness is reached, after which the ear ceases to detect any difference in hearing sensation, *e.g.*, there is a saturation value †, although it may depend to an extent on the maximum pressure of the impulse. Also the possibility of supersonic sounds modifying the aural sensation of audible sounds must not be dismissed without experimental investigation.

Throughout this discussion of transients we have tacitly assumed that the coil is always in a constant radial field.

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* So far as the author is aware.

† Above a certain value there is, of course, the sensation of pain.

A little consideration will show that with a transient consisting of a single pulse, the disk of fig. 1 will move out of the field and not return. Moreover, we postulate that for the purposes of the preceding discussion the coil always moves in a radial field whatever its position in space. In practice it is clear that the disk must be mounted on some form of elastic constraint at its periphery or elsewhere. In this case the equivalent electric circuit is indicated by fig. 3. When the coil is open-circuited, the disk has a natural frequency due to the elastic support; but when the circuit is closed, the resistance of the valve and coil are adequately low to provide large damping, thereby making the system quite aperiodic. It is easy to show that the critical resistance is

$$\frac{1}{2}\left[\frac{L'm}{C'm}\right]^{\frac{1}{2}}.$$

If the natural frequency is sufficiently low, say 3 per second, its effect on the frequency components above 50 cycles can be disregarded.

It is of interest to remark that in an actual moving coil loud speaker with a conical diaphragm, transients due to tympani cause a motion of the coil in one direction or the other which is visible to the eye.

We have made a tacit assumption, namely, that the instrument used for detection does not disturb the pressure distribution of the medium. At frequencies in the neighbourhood of 10,000 cycles the wave-length is so short (about 0·28 cm.) that the human body alters the pressure distribution very materially. The increase in pressure at the higher frequencies caused by diffraction due to the head can be calculated by assuming it to be spherical. Thus the distribution will vary from observer to observer. Moreover, when the variations in aural sensitivity and sensation are added, it is clear that a transient will not sound identical to all observers.

CXV. *A Study of the Three-Electrode Vacuum-Tube Oscillator.—Conditions for Maximum Current.* *By* E. T. CHO, *Ph.D., Indiana University, Bloomington, Indiana, U.S.A.*[*]

THE study is confined to one circuit, the "tuned grid" circuit. This circuit is shown in fig. 1, and consists of a three-electrode vacuum tube (201 A) in the grid circuit of which is connected the oscillating circuit, made up of a coil L and a variable condenser C.

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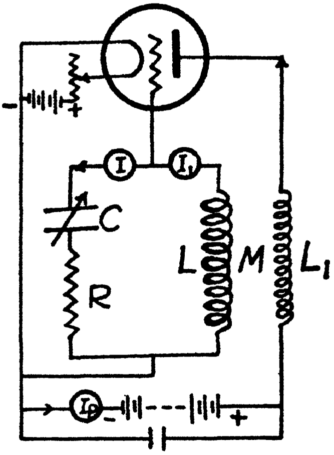
[*] Communicated by Prof. R. R. Ramsey, Ph.D.

In the plate circuit a "tickler" or feed-back coil L_1 is connected in series with a B battery and a D.C. voltmeter. A voltmeter is used as a milliammeter to measure the D.C. component of the plate current. A fixed condenser is placed so as to by-pass the A.C. component of the current around the milliammeter and the B battery. The radio-frequency current is measured by means of a high-frequency ammeter which is placed in series with the variable condenser C. The coils L are made of No. 18 D.C.C. magnet wire, and the coils L_1 are made of No. 34 D.C.C. magnet wire; they are wound on a basket weave form, the diameter of which is about 4 inches.

Fig. 1.



"Tuned grid" circuit.

With a given coil L and a given plate potential and constant filament current the problem is to adjust the condenser C, the inductance of the tickler coil L_1, and the coupling between the coils L and L_1 so as to get the maximum radio-frequency current in the oscillating circuit CLR.

The method of procedure is as follows:—With a given coil L and a tickler coil L_1 the coupling of L and L_1 is fixed, and the capacity C is changed until the radio-frequency ammeter gives the largest reading. Then the coupling between the coils is changed, and the condenser is again changed until the greatest current is obtained. This process is repeated until the coupling is found which gives the largest current. The method is illustrated by the data given in part (*a*) of Table I. The best coupling for coils L and L_1 is marked "max." in the table.

A second coil L_1 is then used as a tickler coil, and the procedure is repeated. A third, fourth, etc. coil is then used in the position L_1 until the best combination to be used with the coil L is found. The data given by part (*b*) of Table I. illustrate the method. The data recorded here correspond to the data marked "max." in part (*a*) of the same table. The data in part (*b*) marked "max. max." give the best values of coil L_1, mutual inductance M, coupling coefficient *k*, and capacity C, to give the maximum-maximum current with the given coil L, with constant plate potential and filament potential.

Table I.

	L.	L_1.	M.	*k*.	I.	C.
(*a*)	3·6	200	14·5	·54	61	·001235
			10·0	·38	67 max.	·001200
			6·0	·22	53	·001140
			3·0	·11	10	·000750
(*b*)	3·6	200	10·0	·38	67	·001200
		100	8·0	·42	113	·001030
		60	8·5	·58	119 max. max.	·000710
		30	5·9	·55	111	·000565

Table II. gives the data for maximum-maximum conditions for sixteen coils, or sixteen values of L, and is a summation of about three thousand separate determinations.

Table II. gives the value for sixteen coils used in the position L. The coils have 2, 3, 4–17 turns of wire. The values of the inductance L, L_1, and M in the tables are expressed in microhenries; the resistance R is expressed in ohms; the current I is expressed in milliamperes; the capacity C is expressed in microfarads; *k* is the coupling coefficient; λ is the wave-length expressed in metres. The wave-length is calculated from the formula $\lambda = 1884 \sqrt{LC}$. These values as calculated are somewhat lower than the actual value of the wave-length as measured with a wave-meter.

The inductances L and L_1 were measured by the wave-meter method by connecting the coil to a calibrated variable condenser and tuning the circuit when it was coupled loosely to an oscillator of known wave-length. The mutual inductances M were measured by clamping the coils L and L_1 so as to hold them rigidly in the same relative position, and then coupling them first in series and measuring the inductance and then connecting them in series opposition and measuring the inductance again. From these two results the mutual inductance M is calculated.

TABLE II.

E_f = 5·5 volts. E_p = 90 volts.

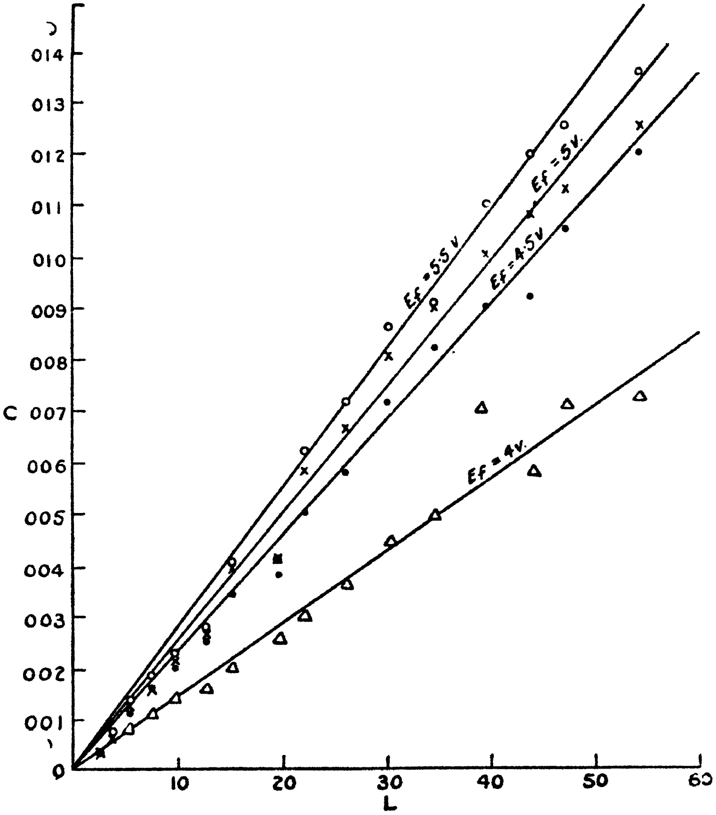
L.	L_1.	R.	*k*.	M.	I.	C.	Wave-length.
2·4	40	—	·52	5·0	100	0·000375	56·5
3·6	60	—	·57	8·5	119	·000710	95·3
5·3	100	—	·67	15·5	125	·001315	157·0
7·4	140	4·6	·64	21·0	135	·001830	218·0
9·7	200	4·2	·43	29·0	138	·002235	277·0
12·6	250	5·0	·62	35·0	138	·002710	349·0
15·4	315	4·6	·60	42·0	136	·004055	471·0
19·7	450	4·6	·53	50·0	137	·004055	566·0
22·3	450	4·6	·70	70·0	146	·006235	702·0
26·4	620	4·5	·62	80·0	145	·007175	816·0
30·3	620	5·0	·73	100·0	142	·008600	960·0
34·9	800	5·0	·60	100·0	145	·009155	1065·0
39·1	990	4·8	·68	135·0	144	·010955	1230·0
44·0	1190	5·0	·63	145·0	144	·011905	1370·0
47·9	1390	5·0	·62	160·0	145	·012500	1460·0
54·5	1390	4·7	·69	109·0	144	·013580	1620·0
Average ...		4·74	·61				

Table II. gives the conditions which give the maximum of maximum current for each of the sixteen coils when placed in the position L_1, when the filament potential E_f was 5·5 volts and the plate potential E_p was 90 volts. It will be noted that the resistance of the oscillating circuit as measured by the resistance variation method is about constant, the average value being 4·74 ohms. A large part of this resistance is due to the milliammeter. It will be noted that the frequency of the current through the small coils is much greater than the frequency of the current in the large coils.

The results have been collected in eleven other tables much like Table II. In these tables the filament potential E_f has had the values 4, 4·5, 5·0, and 5·5 volts; the plate potential E_p had the values 88, 92, and 96 volts; the resistance of the circuit had the values 4·74, 5·74, 6·74, 7·74, and 8·74 ohms. The wave-length varied from 50 to over 1600 metres.

Since the tables are similar to Table II. they are not given here. The results of the twelve tables are shown in figs. 2, 3, and 4.

Fig. 2.



howing that L/C varies as $1/E_f^2$.

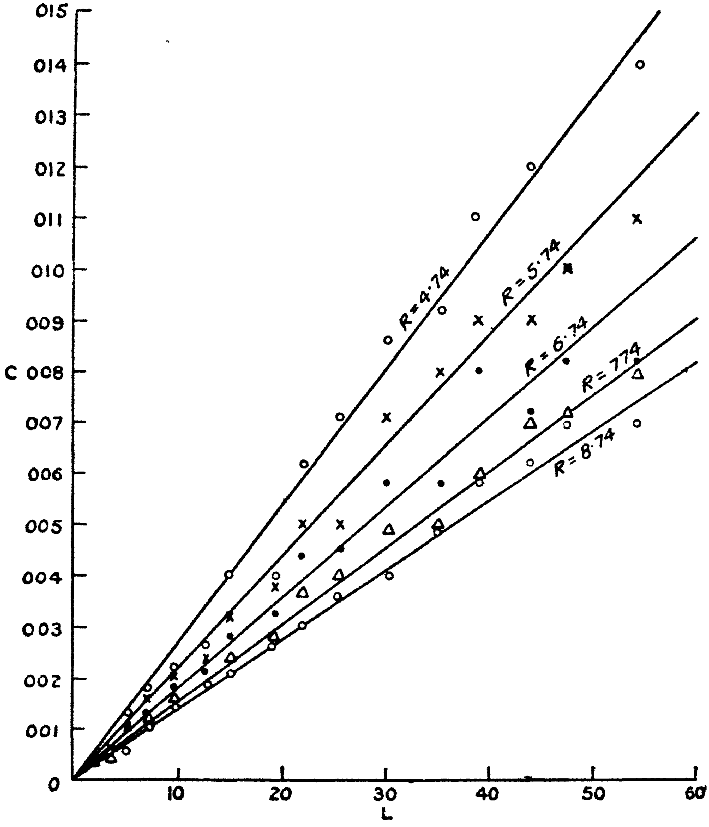
The curve marked $E_f = 5{\cdot}5$ volts is obtained by plotting the data for C and L in Table II. In these data the plate potential E_p was 90 volts and the resistance was about 4·7 ohms.

The three other curves are obtained from data like those in Table II. except that the filament potential has been changed to the values shown in the figure.

Figs. 2, 3, and 4 show the relation of L and C for various values: E_f's, R's, E_p's respectively.

In the figures the points do not fall exactly on straight lines, but the general direction of the points are straight lines. When one considers that the value of the tickler coil L_1 was necessarily changed by steps and the difficulties in getting exact values, the discrepancies can be laid to accidental errors.

Fig. 3.

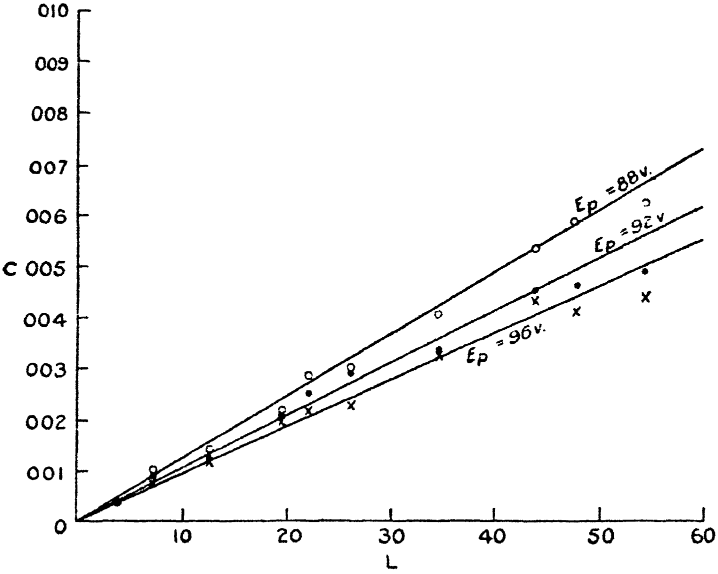


Showing that L/C varies as R.
These curves show the effect of added resistance. $E_p=88$ volts and $E_f=5\cdot5$ volts. The ratio of C to L is constant.

These curves bring out the fact there is a simple relation of the inductance L to the capacity C of the tuned circuit when the constants of the oscillating circuit have been adjusted to give the largest possible current. This relation depends upon the filament and plate potentials and the resistance of the circuit.

In fig. 5 the relation of M and L is shown. The data for this curve are taken when $E_f = 5{\cdot}5$ volts, $E_p = 90$ volts, and $R = 4{\cdot}74$ ohms, and a, amplification constant of the tube, equals 9. This shows that M/L is a constant, about 3·3, which is less than $a/2$; in this case $M/L = {\cdot}74\,a/2$. This suggests that perhaps $M/L = ka/2$, where k is the coupling coefficient.

Fig. 4.



Shows the effect of changing the plate potential of the tube. $R = 8{\cdot}7$ ohms; $E_f = 5$ volts.

Summing up the Experimental Results.

The ratio of L and C for "max. of max." current is some function of R, E_f, and E_p. We may conclude that

L/C varies as $1/E_f$ .... Fig. 2
" " R .... Fig. 3
" " E_p .... Fig. 4

Therefore $L = h'' R E_p C / E_f$., where h' is a constant which for this 201 A tube has a value very near to 50 *.

---

* This value is calculated from the upper line of fig. 2.

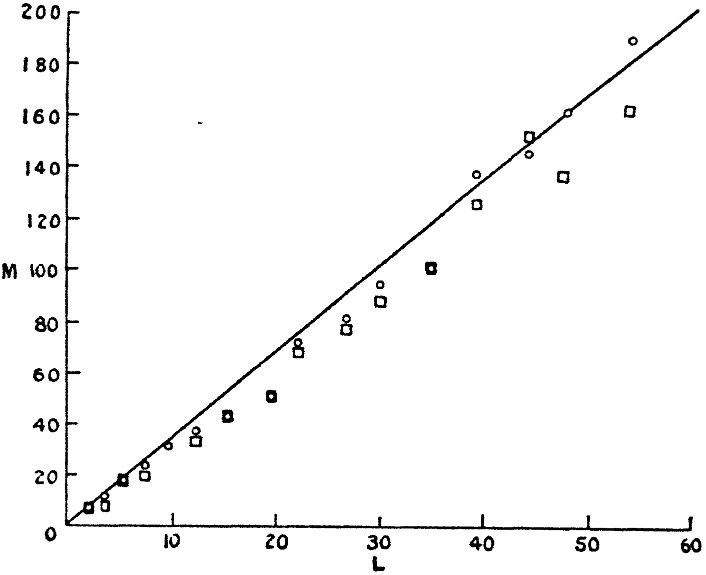
Then

$$L = hC, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (W)$$

where h is a constant depending upon the resistance R, the filament voltage E_f, and plate voltage E_p.

These data and equations can be used to determine the value of the inductances of the coils to give the max. max. current in any given case. As an illustration, suppose it is wished to construct an oscillator to give the maximum amount of current at 300 metres. Assume the resistances and potentials are such as to make the value of h equal 4830.

Fig. 5.



Showing that M/L=constant, which is less than theoretical value $a/2$. The ratio of M to L is nearly constant.

Two sets of data only are plotted. If all the data taken were plotted, the points would not fall farther from the straight line giving the mean value than the points given in the figure do.

The wave-length

$$\lambda = 1884\sqrt{LC},$$

$$300 = 1884\sqrt{LC} = 1884\sqrt{hC^2} = 1884\sqrt{4830}\,C.$$

Solving for C, we have C = 0·0025 mf.

Substituting this value in the equation $L = hC$, we have

$$L = 12{\cdot}1 \text{ mh}.$$

Since from fig. 5 $M/L = 3{\cdot}3$,

$$M = 40{\cdot}0 \text{ mh}.$$

Assuming the coupling coefficient is 0·7, from the relation $M = k\sqrt{LL_1}$,

$$L_1 = 265 \text{ mh}.$$

Theoretical Consideration.

Referring to fig. 1, we have the following equations:— For the plate circuit,

$$E_p = -M\frac{dI_1}{dt} - L_1\frac{dI_p}{dt}; \qquad \text{(I)}$$

for the grid circuit,

$$E_g = -L\frac{dI_1}{dt} - RI_1 - M\frac{dI_p}{dt}, \qquad (2)$$

$$R_pI_p = E_p + aE_g, \qquad (3)$$

where I_p is plate current, E_p is plate potential, I_1 and I are currents in the grid circuit assumed to be equal, E_g is the grid potential, L and L_1 are inductances, R is resistance, M is mutual inductance, a is the amplification constant of the tube, R_p is the plate resistance including the resistance of the voltmeter and coil L_1. By proper manipulation we get

$$\left(\frac{LL_1 - M^2}{R_p}\right)\frac{d^3I}{dt^3} + \left(L + \frac{L_1R}{R_p}\right)\frac{d^2I}{dt^2} + \left(R + \frac{L_1 + aM}{CR_p}\right)\frac{dI}{dt} + \frac{I}{C} = 0. \qquad (4)$$

By assuming that $I = I_0 \sin \omega t$, we have

$$\omega^2 = 1/LC \qquad (5)$$

and

$$-aL/2 - q < M < -aL/2 + q. \qquad (6)$$

Note.—Equations (4), (5), and (6) are derived in several places, one being Morecroft's 'Radio Communication,' p. 597, and need not be derived here.

In order to determine the possible condition of I from equations (1) and (2), multiply (1) by M and (2) by L_1 and subtract the results; we get

$$ME_p - L_1E_g = -M^2\frac{dI_1}{dt} + L_1L\frac{dI_1}{dt} + L_1I_1R,$$

but

$$I_1 = I.$$

Dropping the I_1 and merely writing I. and integrating

$$\frac{-t}{-M^2+LL_1}+h=\frac{\log(L_1RI+L_1E_g-ME_p)}{RL_1},$$

since $t=0$ and $I=0$, therefore the constant h becomes

$$\frac{\log(L_1E_g-ME_p)}{RL_1};$$

then the solution becomes

$$I=\left(\frac{L_1E_g-ME_p}{RL_1}\right)\left(e^{\frac{-L_1Rt}{LL_1-M^2}}-1\right). \quad . \quad . \quad (7)$$

From equation (7), when t becomes infinity, the current I becomes constant and equal to

$$I=ME_p/RL_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where E_g is negligible compared with other quantities. This equation shows the relation between I and M, E_p, L_1, R.

Substituting $k\sqrt{LL_1}$ for M, equation (8) becomes

$$I=\frac{E_pk\sqrt{L/L_1}}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In equation (9), instead of having an independent variable expressed in terms of M, we have it expressed in terms of the coupling coefficient k.

This follows Ohm's law, since the current I is inversely proportional to the resistance. We may write the equation (8) in terms of a by substituting $PaL/2$ for M.

$$I=PaLE_p/2RL_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where P is a constant.

From equations (9) and (10) I becomes

$$I=\frac{E_p(k\sqrt{L/L_1}+PaL/2L_1)}{2R} \quad . \quad . \quad . \quad . \quad (11)$$

From equation (6) the mutual inductance M should be equal to about one-half of the inductance times the amplification constant of the tube for maximum current.

In fig. 5 the average value of $M/L=3\cdot3$, which is less than a divided by 2, since the amplification constant a equals about 9. This curve is plotted from data in which the current is maximum of maximum.

Again the third-order differential equation (4) can be reduced to a second-order equation if we assume that we have close coupling, or that $M^2=LL_1$ and that the value of

L_1R/R_p is very small compared with L. Making these substitutions, the equation becomes

$$L\frac{d^2I}{dt^3}+\left(R+\frac{L_1+aM}{CR_p}\right)\frac{dI}{dt}+\frac{I}{C}=0. \quad . \quad . \quad (12)$$

In order to solve equation (4) we have assumed that $k=$ unity. Table II. shows that, for maximum of maximum current, k has an approximate constant value of 0·61. Then L_1 is relatively small: the value of k approaches unity for maximum current, as is shown in Table III.

TABLE III.

L.	L_1.	M.	k.	I.
19·0	105·0	36·0	·78	58
		27·0	·60	57
		23·0	·51	53
		20·0	·45	53
		16·0	·36	46
		12·0	·27	38

We have shown that M/L is a constant in fig. 5, say b, and from theoretical assumption that $M^2=LL_1$. Then

$$L_1=b^2L.$$

Take equation (10) and express M and L_1 in terms of L. Then we get

$$L\frac{d^2I}{dt^2}+\left(R+\frac{b^2L+abL}{CR_p}\right)\frac{dI}{dt}+\frac{I}{C}=0$$

or $$\frac{d^2I}{dt^2}+(R/L+u/C)\frac{dI}{dt}+\frac{I}{CL}=0, \quad . \quad . \quad (13)$$

where $$u=\frac{b^2+ab}{R_p}.$$

The solution of (13) becomes

$$I=a_1e^{(k'+k'')t}+a_2e^{(k'-k'')t},$$

where $$-\tfrac{1}{2}(R/L+u/C)=k'$$

and $$+\tfrac{1}{2}\sqrt{(R/L+u/C)^2-4/LC}=k''.$$

When $t=0$, $I=0$. Then $a_1=-a_2$, and I becomes

$$I=A(e^{(k'+k'')t}-e^{(k'-k'')t}).$$

When the current is a maximum,

$$\frac{dI}{dt}=0$$

or

$$\frac{dI}{dt}=A[(k'+k'')e^{(k'+k'')t}-(k'-k'')e^{(k'-k'')t}]=0.$$

Since t cannot be zero when the current is a maximum, the only way to make the equation equal to zero is to let k'' be zero.

Equating the value of k'', as given above to zero, expanding, and arranging in terms of powers of C/L and solving, we get C/L = a constant. This constant is expressed in terms of u and R, and is very approximately equal to $-u/R$.

Then

$$L/C=-R/u. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The negative sign is explained when it is remembered that M, the mutual inductance between the coils, is essentially negative.

The numerical value of R/u agrees with the value of h in the experimental equation $L=hC$.

Summary.

(*a*) In the case of the "tuned grid" circuit the equation has been solved, and the equation for the current is

$$I=E_p\left(\frac{k\sqrt{L/L_1}}{R}\right)=(aPL/2L_1)/R.$$

(*b*) In the case of the oscillating circuit made up of a primary coil whose inductance is L, a tickler coil L_1, and a variable condenser, it has been proved experimentally that when the circuit has been adjusted by changing both capacity and the mutual inductance between the coils until the maximum current has been obtained, then M/L = constant, which is somewhat less than the derived theoretical value. This holds true for circuit tuning from 50 to 1600 metres of wavelengths. This relation, as shown by equation (6), is

$$M=aPL/2 \quad \text{or} \quad M/L=aP/2=\text{a constant}.$$

(*c*) The relation between L and C for maximum of maximum current is found by experiment, and is shown in the equations (W) and (14) to be

$$L/C=\text{constant}.$$

The value of the capacity C is much larger than that usually used in practice. These results apply for maximum current and not necessarily for maximum power or maximum efficiency.

CXVI. *The Transmission of Sound through Partitions. II.—Vibrating Partitions. By* A. H. DAVIS, *D.Sc., and* T. S. LITTLER, *M.Sc., Physics Department, The National Physical Laboratory, Teddington, Middlesex* *.

ABSTRACT.

THE paper is a continuation of previous work on the measurement of the transmission of sound through partitions of various materials. In the method the test panel covers an aperture in a sound-proof wall between two rooms. A beam of sound is directed obliquely upon one side of the partition, and upon the other side measurements are made of the sound transmitted. Whilst the earlier work was concerned largely with panels of a felt-like nature, the present paper gives results for partitions—ranging from a sheet of paper to single and double board partitions and to a brick wall—which transmit sound to a greater or lesser extent by vibration. It is found that, in spite of partition vibration, the sound is transmitted as a beam, and measurements of transmission ratio are largely independent of the position in the transmitted beam at which measurements are taken. To reduce errors associated with single-point observations, a moving microphone was found to be advantageous. As an additional aid in avoiding difficulties due to interference systems in the test room, a trial was made of the use of a note of fluctuating frequency.

The results of the measurements of sound transmission through panels of different types and weights are given, and a selection are exhibited graphically.

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1. *Introduction.*

IN a previous paper † the arrangements for measuring the transmission of sound by partitions of various materials were described. The test panel covered an aperture in a sound-proof wall between two rooms. On one side a beam of sound was directed obliquely upon the partition and, at points in the beam on the other side, measurements were made of the sound transmitted. Comparison with the transmission through the uncovered aperture gave the transmission ratio for the partition. The obliquity of the beam and the lagging upon the walls of the source room prevented any reflexion of sound back to the source by the partition or walls, and obviated any acoustic reaction upon the source[*]. The lagging upon the walls, floor, and ceiling of the receiving chamber reduced the intensity of sound outside the main beam, and minimized stationary wave effects.

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* Communicated by the Authors.

† Phil. Mag. iii. p. 177 (1927).

The earlier communication was chiefly concerned with panels of a felt-like nature, and the consideration of solid partitions and of the complications that might arise from their drum-like vibration was reserved until the present paper, which gives results for partitions of various types and weights—ranging from a sheet of paper to a brick wall—which transmit sound to a greater or lesser extent by vibration.

2. *Vibration of Solid Partitions.*

It appears from calculation that transmission through ordinary solid partitions is mainly due to flexural vibration of the panel, not to true acoustical refraction. With this in mind, some experiments were made on partition vibration. It was verified by simply touching the partition lightly with the fingers, that it was actually set in vibration by the sound. By applying an alternating mechanical force of constant magnitude to the central point, and observing the consequent velocity of vibration of the partition for a range of frequencies of the driving force, the curve of fig. 1 was obtained, showing the manner in which the response of a nominal $\frac{3}{8}$-inch fibre board varied with frequency for a mechanical driving force of constant magnitude. Various resonances within the acoustical range were revealed. Somewhat similar results were obtained for two other points of application of the driving force.

The driving of the partition and the measurement of the consequent amplitude of vibration were both carried out by making use of movements of loud-speakers of the type in which a coil of wire moves in the annular field of a pot-shaped magnet. For driving purposes the coil was attached to the partition and the magnet was separately supported. A known alternating current, $I \cos nt$, passed through the coil of length l_1, resulted in a mechanical force. $F = Il_1N_1 \cos nt$, being exerted upon the partition, where N_1 is the radial magnetic flux-density at right angles to the wire of the coil in the annular gap of the electromagnet. To observe the consequent displacement, $A\cos(nt+\alpha)$, of the partition at any point, another coil was attached on the other side of the partition. The motion of this coil (of length l_2) moving in the field N_2 of its magnet, set up an e.m.f. (e) proportional to the velocity of the coil, and given by $e=N_2l_2An\sin(nt+\alpha)$.

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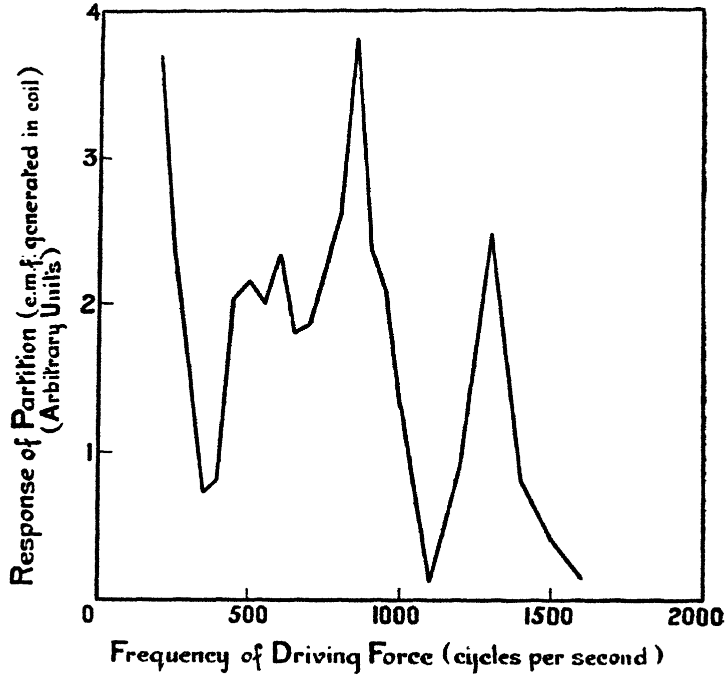
[*] Owing to reaction upon the source when the incident beam was *normal* to the test partition, the apparent transmission through felt at 500 cycles per second was markedly increased (from 50 per cent. to 300 per cent.) by altering the distance of the source from the partition by one quarter of the wave-length of the sound.

Fig. 1.



Response of partition under mechanical forcing.

Thus "e" was a measure of An, a quantity to which pressures and velocities in sound-waves are each proportional. By keeping the current I, and thus the driving force, constant whilst the frequency was varied, the determination of "e" gave a relative measure of the velocity of the partition at the point chosen.

The erection of the apparatus was quite simple. Two moving-coil receivers were taken and a piece of brass rod was screwed into the centre hole of each diaphragm, thus replacing the small bolt used for clamping the diaphragm to the frame upon which the coil is wound. Each rod was securely attached so that the diaphragm, coil, and rod were rigidly connected. On the face of the partition a little hot sealing-wax was applied to points which were to be studied, in order to form a foundation for attaching the brass rods later. Each receiver movement was clamped to a rigid support, and its position adjusted until the end of the brass rod just touched the sealing-wax on the partition. The rod was then securely sealed to the partition by the application of a liberal amount of wax. When both movements were fastened in this way the diaphragm clamping screws were removed, and it was found that each coil moved freely with the partition. Under these circumstances very little constraint was exerted upon the partition by the measuring devices.

3. *Transmission of Sound through Solid Partitions.*

Following the experiments demonstrating partition vibration, measurements were then made of the transmission of sound through the above and other partitions in which vibration was expected to play a prominent part With felt-like partitions it had been found that the effect of covering the aperture had been to reduce the intensity of the transmitted sound in practically the same ratio at all points in the transmission room. This implied primarily that the oblique beam was transmitted unchanged in form. Since, however, the walls of the transmission chamber, although well lagged, were not completely absorbent, it implied also that the residual interference system set up in the chamber through partial reflexion to and fro by its boundaries was not markedly affected by substituting a felt panel for the area of open aperture which formed a portion of one side. It is unlikely that partitions with a hard non-absorbent surface are as satisfactory as felt in this latter respect.

In the present experiments with partitions likely to transmit sound by virtue of their mechanical (drum-like) vibration, it was necessary to ascertain whether the beam was transmitted unchanged in form or whether any appreciable amount of sound was sent out, say, in a direction perpendicular to the panel instead of in continuation of the oblique direction of the incident beam. Such an action would be inconvenient, as transmission ratios would depend upon the point in the room at which they were measured.

A somewhat analogous experiment with water-ripples directed obliquely upon a rubber membrane in a solid wall between two halves of a ripple-tank had shown that beam transmission was possible when the fundamental frequency of the membrane was low *. Moreover, the size of the aperture (5 ft. × 4 ft.) in the acoustical tests of partitions was sufficiently great for the fundamental frequency of the building materials tested to be low compared with the frequency of the sounds concerned †.

In actual tests it was readily verified by ear for all types of partition tested that a pronounced beam was transmitted in the usual oblique direction, and that no undue amount of sound was sent out in other ways. Measurements by microphone further demonstrated that there was always a definite beam in the case of the transmitted sound, intensities at points off the beam being comparatively small.

For the fibre board which had been the subject of earlier tests on vibration, determinations of transmission ratio were made at a number of points off the main beam. As the intensities of sound at these points were relatively small, corresponding to from 3 per cent. to 40 per cent. of the maxima observed in the beam, the points were, of course, of secondary importance as regards the total energy transmitted by the partition. The average transmission ratio determined for a given frequency at points off the track of the beam did not, however, in general differ from that obtained in the main beam by more than 25 per cent. In one case, namely at a frequency of 800 cycles per second, the ratio off the beam was abnormally high, but even in this case a point on the perpendicular through the centre of the partition gave normal values, indicating no special concentration of sound in a direction perpendicular to the partition.

4. *Measurements by Point-to-Point Method.*

In the case of several other partitions, measurements of the transmission ratio were made at a number of points spaced 1 foot apart along the axis of the beam. Results for a frequency of 1000 cycles per second are given graphically in fig. 2 for various distances from the partition. Since the sensation of loudness in the human ear is closely related to the logarithm of the intensity of the exciting sound, a logarithmic scale of intensity is used. For convenience where logarithms are concerned, the reciprocal of the transmission ratio (known as the reduction factor) is employed instead of the transmission ratio itself. It will be seen that, whilst results for the heavier partitions are not so uniform as those for felt, the values for a given partition show no systematic dependence upon the point at which measurements were taken.

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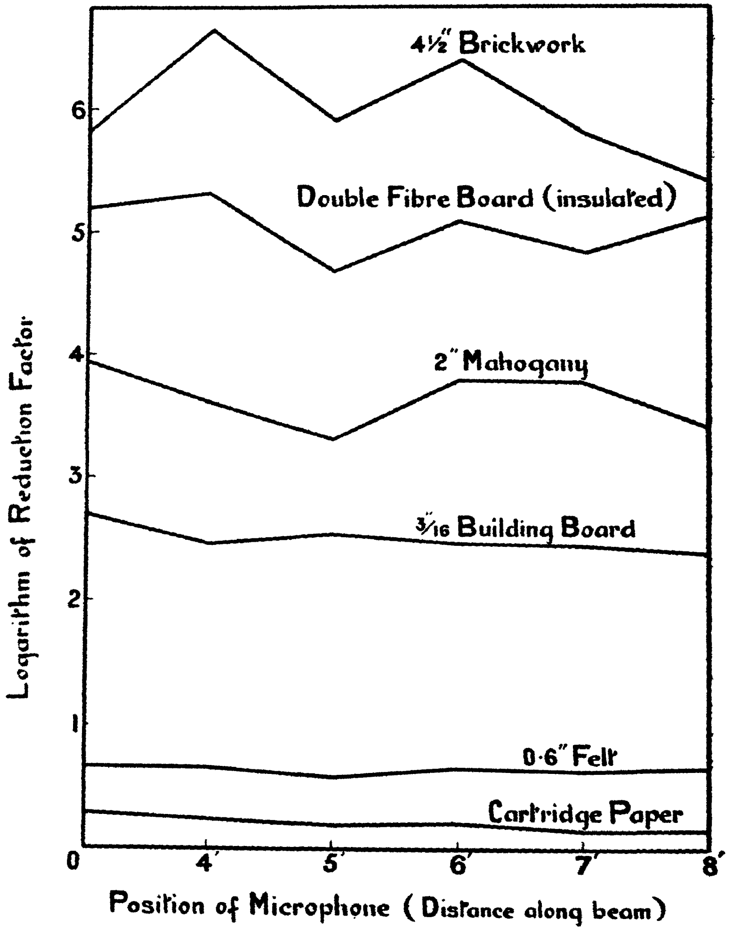
* Davis, Proc. Phys. Soc. 1926.

† This may well prove to be the criterion determining the minimum size upon which tests of practical value may be conducted with building materials.

Fig. 2.



Sound transmission through various partitions measured at a series of positions in the beam.
(Frequency of note—1000 cycles per second.)

On the whole, therefore, it was concluded that the beam was transmitted substantially unchanged in form, but that to reduce errors from various causes it was desirable to take an average of the results obtained at a number of points.

5. *Averaging by Moving Microphone.*

To reduce the work involved in taking averages, experiments were made to test whether they could be obtained automatically by swinging the microphone to and fro along the sound beam in the test room, only the average e.m.f. set up in the cycle being measured.

A rigid suspension system attached to a point near the ceiling of the chamber was arranged for swinging the microphone in a definite manner in a vertical plane along the sound beam, the region thus explored being near to the standard positions at 4, 5, and 6 feet from the aperture. Owing to its harmonic swing, the microphone moves more rapidly through its equilibrium position than through points near the extreme of its excursions, and in consequence the average obtained gives greatest weight to the extreme positions. Accurate reproducibility of swing is thus desirable. Consequently a pointer and scale was erected to facilitate accurate observation of the amplitude of swing, which was maintained constant and of standard magnitude by impulses suitably applied.

Incidentally a second microphone was swung near the source in the other room. Owing to the obliquity of the beam of sound and the lagging upon the walls of the source chamber (see earlier paper) the reading of this microphone was practically the same whether a partition covered the test aperture or not. Consequently it serves in tests as a convenient check upon the constancy of the loud-speaker from day to day and week by week, a detail which is sometimes important.

For measuring the e.m.f. from the microphone an arrangement involving an amplifier and a detector was used. As detector, an instrument—such as a vacuo thermojunction—having sluggish action and square-law characteristics would be very suitable; for it would give minimum fluctuations of galvanometer deflexion and, in averaging the square of acoustical amplitude, would thus be averaging the sound-energy. Actually, in spite of its speedier response, a crystal detector was employed, on account of its greater sensitiveness and robustness; it had approximate square-law characteristics.

To compare the results obtained by a swinging microphone with those due to point-by-point calculation, measurements of sound transmission were made by the two methods both for a compressed building board and for a 4½-inch brick wall. In all cases the figures due to the swinging microphone lay within the limits of variation of individual measurements in the point-to-point exploration, of which some idea has been given in fig. 2. The actual results of the comparisons are included in Table I. later, where the two sets of results for each partition (Nos. 11 and 26) are given in juxtaposition. For the compressed board the differences are barely sufficient to be ordinarily detected by ear. For the brick wall wider variations occur, but the sound reduction is so much greater that the variations are not very serious from a practical point of view.

6. *Use of Sound Source of Variable Frequency.*

As an additional aid in avoiding difficulties due to the residual interference system which had survived the application of lagging to the walls of the receiving room, trial was made of the use of a test-note of variable pitch. This note was obtained from a loud-speaker operated by a valve oscillator, the tuning circuit of which contained a variable inductance driven by means of an electric motor. By this device the frequency of the note varied cyclically by ± 10 per cent. some 25 times per second.

The arrangements adopted greatly reduced the residual interference system in the transmitted beam, and were used in a few tests.

It appeared, however, that the moving microphone in the lagged room was generally satisfactory with a pure note of fixed frequency, and as there are some disadvantages in the use of the variable note in present circumstances, the fixed note was ordinarily used in the tests. It was noted, for instance, that, with the variable note, resonances in the loud-speaker and microphone gave undue prominence to certain sources in the frequency band, so that the e.m.f. from the microphone was often very different from that of the electrical current driving the loud-speaker and from that of the sound. There was, consequently, some uncertainty—although perhaps not serious—in the character of the test-note. Moreover, with a single pure note it is quite legitimate to employ sharply-tuned measuring apparatus and circuits—an important consideration where parasitic electrical effects from outside sources in the neighbourhood of the chambers have to be circumvented

7. *Results and Tables.*

Results obtained for the transmission of sound through a number of materials and structures are given in Table I., the figures tabulated being the logarithms of the reduction factors of the partitions tested. Table II. is useful for converting logarithms of reduction factors to transmission ratios, and *vice versa*.

As explained earlier, the logarithmic figure is convenient on account of the close relation the sensation of loudness bears to the logarithm of the intensity of the sound concerned. The "reduction factor" is defined as the reciprocal of the "transmission ratio," this latter being the ratio between the quantities of sound energy transmitted through the test partition and through the uncovered aperture when the partition is removed.

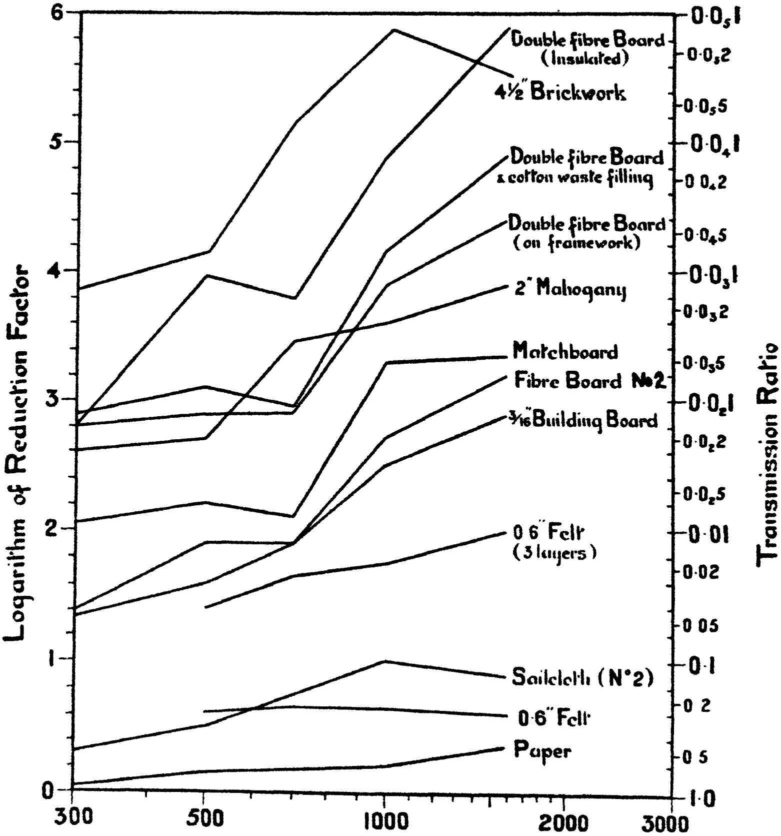
The logarithms of the reduction factors are given to the nearest 0·05. This corresponds to practically the smallest loudness-change detectable by ear, even when the change-over between the sounds to be compared is instantaneous, and no difficulties with interference systems or with extraneous noise are involved. In practice larger differences of 0·1 or 0·2 are of little importance; as will be seen from Table I. (No. 9), they correspond only to the slight difference in loudness that can be caused by covering an open doorway with a sheet of paper. It requires a partition for which the logarithm of the reduction factor is about 6 to reduce to inaudibility a sound having the loudness of an ordinary voice.

The partitions tested cover a wide range of transmission ratio, varying from a transmission of some 5–35 per cent. for cartridge paper to a few parts in a million for a brick wall. Fig. 3 presents graphically the results for a selected number of the partitions. A scale of ordinates has been included to the right of the graph so that transmission ratios may be read off if desired. In general, with the single non-porous partitions, the heaviest transmitted least sound.

Among the results may be noted figures for sailcloth of various types, this being a material sometimes used as a velarium for acoustic purposes in large halls. At 300 and 1600 cycles per second the light sailcloth transmitted respectively twice and six times as much sound as the heavy sailcloth.

Values for some simple compressed building boards are included. A certain fibre board was tested as a single board clamped over the aperture, as a double partition with one layer of board on each side of a 4-inch wooden framework, as a double partition with the frame filled with absorbent (cotton waste), and as a double partition composed of two completely insulated boards. In the latter case one sheet of

Fig. 3.



Sound transmission through a variety of partitions for a series of notes of different frequencies.

fibre board was clamped over one face of the test-aperture, and another over the other face. As the two were thus, in fact, mounted upon the separate 9-inch brick walls which constitute the separation between the two test-rooms, they were thoroughly insulated from each other. The air-space between them was 23 inches thick. In such a case the results show that each of the two insulated boards tends to have its full effect, the logarithm of the reduction factor for the two being of the order of the sum of the values for the separate boards. For some frequencies, however, the double partition falls short of this full effect, possibly through resonances of the intervening air, or even perhaps through differences of fixing in the erection of the boards. A layer of quilt hung in the interspace appeared to increase the insulation. Roughly speaking, the double-fibre board on a 4-inch frame gave results on the logarithmic scale lying half way between those for a single board and for two insulated boards. Filling the interspace with cotton waste slightly, but consistently, decreased the sound transmitted.

Figures for a 2-inch mahogany board, for a ⅝-inch mahogany-faced plywood, and for matchboard fall intermediate between those for the single-fibre board and the double-fibre board on framework. One the whole, the single-brick wall is superior to the other constructions tested.

The authors desire to thank Dr. G. W. C. Kaye, Superintendent of the Physics Department, for continued interest and suggestions. Mr. W. J. B. Elliott, Junior Observer, again assisted with the experimental work.

TABLE I.

Sound Transmissions through Partitions.

Partition.				Logarithm of Reduction Factor for Frequency (cycles per sec.).					Method of Test.
No.	Description.	Thickness (in.).	Weight (lb. per sq. ft.).	300	500	700	1000	1600	
	A. Partitions clamped over aperture.								Paragraph No.
1.	Blanket.	—	—	—	—	0·20	—	—	4
2.	Felt (1 layer).	0·6	0·6	—	0·60	0·65	0·65	0·60	4
3.	Felt (2 layers).	1·2	1·2	—	1·05	1·15	1·15	1·20	4
4.	Felt (3 layers).	1·8	1·8	—	1·40	1·65	1·75	2·00	4
5.	Felt (4 layers).	2·4	2·4	—	1·85	2·05	2·30	2·65	4
6.	Sailcloth No. 1.	0·037	0·14	0·45	0·85	—	1·45	1·50	5
7.	Sailcloth No. 2.	0·025	0·09	0·30	0·50	—	1·0	0·90	5
8.	Sailcloth No. 3.	0·025	0·07	0·10	0·40	—	0·90	0·70	5
9.	Cartridge paper.	0·0088	0·031	0·05	0·15	—	0·20	0·35	4
10.	Eelgrass quilt.	0·5	0·20	—	—	0·50	—	—	4

TABLE I. (*cont.*).

Partition.				Logarithm of Reduction Factor for Frequency (cycles per sec.).					Method of Test.
No.	Description.	Thickness (in.).	Weight (lb. per sq. ft.).	300	500	700	1000	1600	
11.	Compressed board.	0·19 0·19	0·61 0·61	1·35 1·40	1·60 1·60	1·90 2·0	2·50 2·55	2·90 2·85	4 5
12.	Mahogany-faced ply-wood.	0·6	1·4	2·10	2·40	3·30	3·30	3·80	4
13.	Mahogany.	1·85	4·9	2·60	2·70	3·45	3·60	3·90	4
14.	Fibre board No. 3.	0·29	0·46	1·05	1·65	1·65	2·45	3·10	4
15.	Fibre board No. 2.	0·46	0·66	1·40	1·90	1·90	2·70	3·20	4
16.	Fibre board No. 1.	0·50	0·75	1·55	1·90	1·95	2·90	3·40	4
17.	Fibre board No. 4.	0·42	0·57	—	1·65	2·0	2·60	2·60	6*
18.	Fibre boards Nos 3 and 4, with layer of eelgrass quilt sandwiched between.	—	—	1·10	2·55	2·45	—	2·75	5
19.	Double-fibre boards Nos. 2 and 4, insulated by an air-space 23 in. wide.	—	—	2·80	4·0	3·80	4·90	5·90	4
20.	Double fibre boards Nos. 3 and 4, insulated by an air-space 23 in. wide.	—	—	—	3·75	3·90	4·55	4·75	6*
21.	As 20, but with a layer of eelgrass quilt hung loosely in interspace.	—	—	—	3·85	5·45	5·95	5·45	6*
B.	*Partitions on framework of* 1½ in. *wood*, 62×46×4½ in. *in size, built into aperture.*								
22.	Double-fibre boards Nos. 2 and 4.	—	—	2·80	2·90	2·90	3·90	4·40	5
23.	As 22, but interspace filled with cotton waste (1·3 lb./sq. ft.).	—	—	2·90	3·10	2·95	4·15	4·90	5
24.	Matchboard. Each strip 46×5×½ in.	—	1·31	2·05	2·20	2·10	3·30	3·35	5
25.	Double matchboard. Each strip 46×5×½ in.	—	—	3·25	2·75	2·90	4·35	4·90	5
C.	*Brick panels built into above wooden framework in aperture.*								
26.	Fletton bricks and lime mortar.	4½ 4½	41 41	3·85 3·75	4·15 4·00	5·15 5·35	5·90 5·90	5·50 5·10	5 4
27.	Fletton bricks and lime mortar (replaced in aperture; fine cracks visible).	4½	41	—	—	5·05	5·80	5·40	5

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* For these experiments the frequency of the test-note varied cyclically over a frequency band lying within ±10 per cent. of the mean frequency.

TABLE II.

For use in conversions involving Transmission Ratios (t), Reduction Factors ($R=1/t$), and Logarithms of Reduction Factors ($\log_{10}R$).

The table gives the first two significant figures of the *transmission ratio* and of the *reduction factor* corresponding to given values of the *logarithm of the reduction factor*.

Mantissa of $\log_{10}R$.	Significant figures of	
	t.	R.
·00	10	10
·05	89	11
·10	79	13
·15	71	14
·20	63	16
·25	56	18
·30	50	20
·35	45	22
·40	40	25
·45	35	28
·50	32	32
·55	28	35
·60	25	40
·65	22	45
·70	20	50
·75	18	56
·80	16	63
·85	14	71
·90	13	79
·95	11	89

R=reduction factor. t=transmission ratio.

Examples:—

$\log_{10}R=0·20.$ $t=0·63.$ $R=1·6$

$\log_{10}R=4·20.$ $t=0·0_4 63.$ $R=1·6\times10^4.$

$\log_{10}R=5·20.$ $t=0·0_5 63.$ $R=1·6\times10^5.$

Note the general relation between the characteristic of $\log_{10}R$ and the number of noughts after the decimal place in t. The only exception is when the logarithm is an exact integer; thus:

$\log_{10}R=5·00.$ $t=0·0_4 10.$ $R=10^5.$

CXVII. *Critical Stresses for Tubular Struts.*
By H. CARRINGTON, *D.Sc.* [*]

A SOLUTION of the problem of the stability of tubular struts with thin walls has been given by R. V. Southwell [†], who deduced two formulæ giving the stresses at which instability occurs whilst the axis of the strut remains straight. One of these gives the stress which will cause a symmetrical distortion such that the lengths of diameter in any axial plane vary in a sinusoidal manner, the cross-section of the strut remaining circular. The other gives the stresses which correspond with lobed types of deformation, or those in which the lengths of diameters in both axial and cross-sectional planes vary in a sinusoidal manner. The latter formula has recently been stated to be incorrect by A. Robertson [‡], who maintained that the minimum collapsing stresses corresponding with the lobed types of deformation are either the same as, or higher than, that for the symmetrical type; whereas Southwell's formula for lobed types of deformation gives stresses which are less than that for the symmetrical type. It will here be demonstrated that Robertson's claim regarding the incorrectness of Southwell's formula is not justified.

It will first be shown briefly how the before-mentioned formulæ were deduced from Southwell's general equation. This is:

$$\begin{aligned}\psi^2\left[\frac{m+1}{2m}k^2q^4\right]&+\psi\left[\frac{m-1}{2m}q^2\{(k^2+q^2)^2+k^2\}\right]\\&+\left(1-\frac{1}{m^2}\right)\frac{m-1}{2m}q^4+\frac{1}{3}\frac{t^2}{a^2}\psi q^2\left[\frac{m+1}{2m}k^2\{(k^2+q^2)^2-k^2\}\right.\\&\left.+\frac{m-7m+4}{2m^2}k^2q^2+\frac{m-1}{m}q^4\right]+\frac{1}{3}\frac{t^2}{a^2}\frac{m-1}{2m}\left[(k^2+q^2)^4\right.\\&-\frac{q^6}{m}-k^2\left(2k^4+7k^2q^2+\frac{7m^2+m-2}{m^2}q^4\right)\\&\left.+k^4+3k^2q^2+2\frac{m^2-1}{m^2}q^4\right]=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)\end{aligned}$$

where $\psi=-\frac{m^2-1}{m^2}\frac{p}{\mathrm{E}}$, p = stress, E = Young's modulus,

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[*] Communicated by the Author.

[†] Phil. Trans. Roy. Soc. A, ccxiii. p. 187 (1913).

[‡] Proc. Roy. Soc. A, cxxi. p. 558 (1928).

$\frac{1}{m}$ = Poisson's ratio, k = number of lobes, $q=\frac{2\pi a}{\lambda}$, λ = wave length of a lobe, a = mean radius of tube, and t = half-thickness of tube.

Taking first the terms which are independent of t^2, as was done by Southwell, and neglecting the square of ψ—, which must be small, we find

$$-\psi=\frac{m^2-1}{m^2}\,\frac{q^2}{(k^2+q^2)^2+k^2}. \quad . \quad . \quad . \quad . \qquad (2)$$

If k is zero, it is easy to see that q must be great since ψ must be small. It will also be seen that if $k>0$, the condition that ψ must be small is satisfied if q is small, but that this condition may also be satisfied if q is great. If $k=0$, equation (1) becomes

$$-\psi=\frac{1}{q^2}\,\frac{m^2-1}{m^2}+\frac{1}{3}\frac{t^2}{a^2}\left(2\psi+q^2-\frac{1}{m}+\frac{2}{q^2}\,\frac{m^2-1}{m^2}\right). \qquad (3)$$

Remembering that ψ must be small, it is easily found that the minimum value of p is

$$p=2\mathrm{E}\frac{t}{a}\sqrt{\frac{1}{3}\,\frac{m^2}{m^2-1}}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

the corresponding value of q being given by

$$q^4=3\frac{a^2}{t^2}\,\frac{m^2-1}{m^2}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

In deducing the formula for the lobed type of distortion, Southwell considered only the case where q is small. If $k>0$ and q is small, the important terms in equation (1) are

$$\psi q^2k^2(k^2+1)+\frac{m^2-1}{m^2}\,q^4+\frac{1}{3}\frac{t^2}{a^2}\,k^4(k^4-2k^2+1)=0, \qquad (6)$$

from which the minimum value of p is found to be

$$p=2\mathrm{E}\frac{t}{a}\sqrt{\frac{1}{3}\,\frac{m^2}{m^2-1}}\left\{\frac{k^2-1}{k^2+1}\right\}, \quad . \quad . \quad . \qquad (7)$$

the corresponding value of q being given by

$$q^4=\frac{m^2}{m^2-1}\,\frac{k^4(k^2-1)^2}{3}\,\frac{t^2}{a^2}. \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

Formula (7) is Southwell's formula for lobed types of distortion. There is, however, the possibility that the case where q is great may yield smaller results than those given by formula (7). Neglecting the unimportant terms in equation (1). when $k > 0$ and q is great, it becomes

$$\psi q^2(k^2+q^2)^2+\frac{m^2-1}{m^2}q^4+\frac{1}{3}\frac{t^2}{a^2}(k^2+q^2)^4=0. \quad . \quad (9)$$

The minimum value of this is

$$p=2\mathrm{E}\frac{t}{a}\sqrt{\frac{1}{3}\frac{m^2}{m^2-1}}. \quad . \quad . \quad . \quad . \quad (10)$$

The condition for this minimum is that q should have values given by

$$q=\frac{1}{2}\left\{\sqrt[4]{\frac{1}{\mathrm{A}}}\pm\sqrt{\left(\frac{1}{\mathrm{A}}\right)^{\frac{1}{2}}-4k^2}\right\}. \quad . \quad . \quad (11)$$

If $k^2 > \frac{1}{4\sqrt{\mathrm{A}}}$, the minimum value of p is greater than is given by (10).

Formula (10) is Robertson's formula for lobed types of distortion, and is exactly the same as Southwell's formula (4) for the symmetrical type.

It might here be noted that if $k=1$, Southwell's formula (6) reduces to Euler's formula for the buckling of a long tube where the axis does not remain straight after distortion of the tube. This case need not be considered further.

It is easily seen that Southwell's formula (7) gives smaller values for the critical stresses than Robertson's formula (10). For instance, if $m=2$ in (7) the value of p is only three-fifths of that given by (10). Formula (7) is therefore the more important.

In order to show conclusively that formula (7) is correct, it was decided to work out equation (1) in its entirety for two values of $\frac{t}{a}$. In Tables I. and II. $\frac{t}{a}=0{\cdot}001$ or $0{\cdot}02$ $m=\frac{10}{3}$, and $\mathrm{E}=3\times10^7$ lb./in.². Four-figure logarithms were used throughout the calculations.

Columns A were calculated, using Southwell's formula (7) and the values of q from his formula (8). These values of q were then used in equation (1) and the results tabuated in column B. For the cases where $k=0$, formula (4), which is the same as Robertson's formula (10), and formula (5) were used instead of (7) and (8). The term containing ψ^2 in equation (1) was included in the calculation of the values in column B, but its influence was found to be negligible. The lengths of half waves or values of $\frac{\lambda}{2}$ are also given in the tables for a tube 1 inch in mean diameter. The lengths for tubes of other diameters are, of course, directly proportional to these.

TABLE I.

k.	A. Tons/in.^{2}.	B. Tons/in.^{2}.	q.	$\frac{\lambda}{2}$ (in.) ($a=\frac{1}{2}$ in.).
0	16·21	16·21	40·65	0·07728
2	9·727	9·730	0·08521	36·86
3	12·97	12·99	0·2087	15·05
4	14·31	14·33	0·3812	8·242
5	14·96	14·99	0·6026	5·213
6	15·34	15·37	0·8733	3·597
8	15·71	15·81	1·563	2·011
10	15·89	16·03	2·447	1·283

$$\frac{2t}{a}=0{\cdot}002.$$

TABLE II.

k.	A. Tons/in.^{2}.	B. Tons/in.^{2}.	q.	$\frac{\lambda}{2}$ (in.) ($a=\frac{1}{2}$ in.).
0	324·2	323·7	9·088	0·3456
2	194·5	198·9	0·3811	8·243
3	259·4	269·9	0·9335	3·365

$$\frac{2t}{a}=0{\cdot}04.$$

It will be seen that agreement between the results in columns A and B is close. For the case $\frac{2t}{a}=0{\cdot}002$, when $k=10$ the difference is less than 1 per cent., and for the case $\frac{2t}{a}=0{\cdot}04$, when $k=3$ it is about 4 per cent. For the other cases given the differences are less than these.

In the light of the preceding investigation and the results given in Tables I. and II., it is inferred that Robertson's claim regarding the inaccuracy of Southwell's formula (7) is not justified. As a consequence of this claim, Robertson also mentioned that one of Southwell's diagrams (his fig. 6, p. 235) is incorrect. On comparing this diagram with the results given in Table II., it will be evident that this is not the case.

The problem has also been solved by J. Prescott [*] and W. R. Dean [†], who deduced formulæ similar to numbers (4) and (7).

CXVIII. *On the Vacuum Bolometer as used in Measurements of Solar Radiation.* *By* N. Fairclough, *B.Sc.*[‡]

1. THE fundamental work on the Solar Constant carried out at the Astrophysical Observatory of the Smithsonian Institution is well known. Measurements of the solar radiation are made with the instrument known as the vacuum bolometer, and it is the object of the present paper to investigate a problem arising in the theory of the instrument[§]. The bolometer consists essentially of a delicate electrical thermometer, the sensitive parts being two fine tapes of metal, blackened on the front surface. One tape can be exposed to the sun's rays to be measured, while the other tape is screened from those rays. The tapes are joined by suitable resistance coils, and the whole made up into a Wheatstone's bridge. A small change in temperature in the exposed strip changes the resistance of that strip, and produces a deflexion of the sensitive galvanometer in the circuit. Prof. S. Chapman, F.R.S., suggested to the writer the desirability of investigating what is the best thickness of tape to be used in the instrument, and the following simple argument shows that there will in fact be an optimum thickness which makes the instrument most sensitive.

The tapes of fixed length and width, any temperature change in the exposed tape, due to a fixed amount of radiation, will depend upon the thickness of the tape. If extremely thin tapes are considered they will have very high resistances, and but very small currents will pass through each tape. On exposure, when the balance in the bridge is destroyed, the current passing through the galvanometer, and so the galvanometer deflexion, will be negligible. The current required for extremely thick tapes will be very large, but the tapes will have very low resistances, and, on exposure, the change in resistance will be small. The fraction of current through the galvanometer will be minute, and again we may expect a negligible deflexion. It may be inferred that between these extremes there is a thickness of tape that will give a maximum galvanometer deflexion.

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[*] 'Applied Elasticity,' p. 530 (1924).

[†] Proc. Roy. Soc. A, cvii, p. 734 (1925).

[‡] Communicated by Prof. E. A. Milne, F.R.S.

[§] Annals of the Astrophysical Observatory of the Smithsonian Institution, iv. p. 45.

2. *Nature of the Problem.*

Experimental work at the Astrophysical Observatory of the Smithsonian Institution has defined the best length and width of tape to use, namely, 1·6 cm. and 0·01 cm. respectively *. Accordingly, on this assumption, it will be the object of this paper to investigate what thickness of tape will render the bolometric apparatus most sensitive to solar radiation. The calculations will be applied to platinum tapes of rectangular cross-section. A few calculations of a similar kind have already been given by the Smithsonian observers (*loc. cit.*), but the present investigation is more complete.

The measure of the sensitiveness of the bolometer will be the magnitude of the galvanometer deflexion when the tape is exposed. Any deflexion, z, will depend upon C_g, the current passing through the galvanometer, and the resistance, g, of the instrument. If r_1=resistance of tape to be exposed, r_3=resistance of concealed tape, r_2, r_4 the resistances of the balancing coils; then

$$C_g = f(r_1).$$

Also, there is one particular value of g for which the galvanometer deflexion is a maximum, subject to the remaining resistances in the bridge being constant. Thus, if n=thickness of tape, we require for an optimum thickness

$$\frac{d}{dn}\left[\left(\frac{dz}{dr_1}\right)_{r_1=\frac{r_2}{r_4}.r_3}\right] = 0, \quad . \quad . \quad . \quad . \quad (1)$$

subject to the condition

$$\frac{d}{dg}\left[\left(\frac{dz}{dr_1}\right)_{r_1=\frac{r_2}{r_4}.r_3}\right] = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which fixes the value of g.

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* Annals of the Astrophysical Observatory of the Smithsonian Institution, iv. p. 46.

3. *Steady State of Temperature along the Tape.*

(a) *No external radiation.*

Let θ=temperature of the bolometer tape in absolute degrees at a distance x from the centre. Let $2l, m$ be the length and width of the tape respectively, k the thermal conductivity, and γ the specific electrical conductivity of the material of the tape. Let σ=Stefan's constant of radiation, i=the electric current flowing through the tape in the steady state, and θ_1=the absolute temperature at $x=l$. We assume this to be the temperature of the surroundings.

For tapes *in vacuo*, perfectly black on that face which receives the solar radiation, and perfectly reflecting on all others, there are three factors which combine to determine the temperature across any section. Consider a section of the tape of length δx, at the point x. The exchange of heat consists of

(i.) gain by conduction: this amounts to $kmn\frac{d^2\theta}{dx^2}.\delta x$;

(ii.) gain by generation of heat by the current: this amounts to $(0{\cdot}24\,i^2/\gamma mn)\delta x$, where i is measured in practical units;

(iii.) loss by radiation: this amounts to $\sigma(\theta^4-\theta_1^4)m.\delta x$, where σ is measured in calories per cm.^{2} per second.

In the steady state the gain and the loss must balance, and we have the equation

$$kmn\frac{d^2\theta}{dx^2}+\frac{0{\cdot}24\,i^2}{\gamma mn}-\sigma(\theta^4-\theta_1^4)m=0 \quad . \quad . \quad (3)$$

or

$$\frac{d^2\theta}{dx^2}-A\theta^4+B=0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$A=\frac{\sigma}{kn} \quad \text{and} \quad B=\frac{0{\cdot}24\,i^2}{k\gamma m^2n^2}+\frac{\sigma\theta_1^4}{kn}.$$

In any particular case A is constant, but B depends on γ, which itself depends on θ. To facilitate the integration of equation (4), we shall treat B, and therefore γ, as constant, and the value chosen will be the value of γ at the mean temperature over the tape. In a later part of the paper we shall investigate to what extent this assumption is in error.

If θ_0 = the absolute temperature at the middle of the tape equation (4), on integration, becomes

$$\frac{1}{2}\left(\frac{d\theta}{dx}\right)^2 - \tfrac{1}{5}A\theta^5 + B\theta = -\tfrac{1}{5}A\theta_0^5 + B\theta_0,$$

since

$$\frac{d\theta}{dx} = 0 \quad \text{and} \quad \theta = \theta_0 \quad \text{at} \quad x = 0.$$

Therefore

$$\frac{d\theta}{dx} = -\left[2B(\theta_0-\theta) - \tfrac{2}{5}A(\theta_0^5-\theta^5)\right]^{\frac{1}{2}}$$

or

$$x = \int_{\theta}^{\theta_0} \frac{d\theta}{\left[2B(\theta_0-\theta) - \tfrac{2}{5}A(\theta_0^5-\theta^5)\right]^{\frac{1}{2}}} \quad . \quad . \quad . \quad (5)$$

The boundary condition is $\theta=\theta_1$, the external temperature at $x=l$, so that

$$l = \int_{\theta_1}^{\theta_0} \frac{d\theta}{\left[2B(\theta_0-\theta) - \tfrac{2}{5}A(\theta_0^5-\theta^5)\right]} \cdot \quad . \quad . \quad (6)$$

This equation determines the value of B for chosen temperatures θ_0, θ_1, and equation (5) will give the value of θ at any point x on the tape.

(b) *When external radiation of amount* R *per unit area falls on the tape.*

The resistance of the tape will now be increased. Let γ' be the new value of γ, and let i' be the new current. If θ' be the new temperature at the point x, we have, for the steady state of temperature along the tape, the equation

$$kmn\frac{d^2\theta'}{dx^2} + \frac{0{\cdot}24\, i'^2}{\gamma' mn} - \sigma(\theta'^4 - \theta_1^4)m + Rm = 0 \quad . \quad (7)$$

or

$$\frac{d^2\theta'}{dx^2} - A\theta'^4 + B' = 0, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where A is as before, and

$$B' = \frac{0{\cdot}24\, i'^2}{k\gamma' m^2 n^2} + \frac{\sigma\theta_1^4}{kn} + \frac{R}{kn};$$

so that

$$x = \int_{\theta'}^{\theta_0'} \frac{d\theta'}{\left[2B'(\theta_0'-\theta') - \tfrac{2}{5}A(\theta_0'^5-\theta'^5)\right]^{\frac{1}{2}}} \quad . \quad . \quad (9)$$

if θ_0' = the new central temperature.

Considering the whole length of tape with the appropriate boundary condition,

$$l=\int_{\theta_1}^{\theta_0'}\frac{d\theta'}{[2B'(\theta_0'-\theta')-\frac{2}{5}A(\theta_0'^5-\theta'^5)]^{\frac{1}{2}}}. \quad . \quad (10)$$

This equation determines the value of B′ for chosen temperatures θ_0', θ_1, when equation (9) will give the new temperature θ' at the point x.

In equation (6) put $\theta=\theta_0.t$. Then, writing $\theta_1=\theta_0.\alpha$,

$$l=\int_\alpha^1\frac{(\theta_0)^{\frac{1}{2}}.dt}{[2B(1-t)-\frac{2}{5}A\theta_0^4(1-t^5)]^{\frac{1}{2}}}$$

$$=\int_\alpha^1\frac{(\theta_1)^{\frac{1}{2}}.dt}{[\alpha]^{\frac{1}{2}}[2B(1-t)-\frac{2}{5}A\frac{\theta_1^4}{\alpha^4}(1-t^5)]^{\frac{1}{2}}}.$$

As B increases for a fixed α, this integral decreases. Since it is constant and equal to l, as B increases α must decrease; that is, $\theta_0'>\theta_0$.

4. *Transformation of Equations for the Steady State.*

We have seen that external radiation falling on the tape will produce a rise in temperature at any point. There will be a mean rise in temperature, $\overline{\delta\theta}$, and on this the calculations of galvanometer deflexions for varying thicknesses of tape will be based. To obtain equations (5), (6), (9), (10) in forms more suitable for computation, we have, from equation (5),

$$x=\int_\theta^{\theta_0}\frac{d\theta}{\left[\frac{2A}{5}(\theta_0-\theta)\left(\frac{5B}{A}-\frac{\theta_0^5-\theta^5}{\theta_0-\theta}\right)\right]^{\frac{1}{2}}}$$

or

$$qx=\int_\theta^{\theta_0}\frac{d\theta}{\left[(\theta_0-\theta)\left(\lambda-\frac{\theta_0^5-\theta^5}{\theta_0-\theta}\right)\right]^{\frac{1}{2}}}$$

if

$$q=\left(\frac{2A}{5}\right)^{\frac{1}{2}}=\left(\frac{2\sigma}{5kn}\right)^{\frac{1}{2}} \quad \text{and} \quad \lambda=\frac{5B}{A}=5\left(\frac{0{\cdot}24\,i^2}{\gamma_M m^2 n\sigma}+\theta_1^4\right), \quad . \quad . \quad . \quad (11)$$

where γ_M is used to denote the value of γ at the mean temperature over the tape. Putting $\theta_0-\theta=y^2$,

$$qx=\int_0^{(\theta_0-\theta)^{\frac{1}{2}}}\frac{2dy}{[\lambda-(\theta_0^5-\theta^5)/(\theta_0-\theta)]^{\frac{1}{2}}}. \quad . \quad . \quad (12)$$

From equation (6),

$$ql = \int_0^{(\theta_0-\theta_1)^{\frac{1}{2}}} \frac{2dy}{[\lambda-(\theta_0{}^5-\theta^5)/(\theta_0-\theta)]^{\frac{1}{2}}} \quad . \quad . \quad . \quad (13)$$

Similarly, from equations (9) and (10), on changing the variable from θ' to θ,

$$qx = \int_0^{(\theta_0'-\theta)} \frac{2dy}{[\lambda'-(\theta_0'^5-\theta^5)/(\theta_0'-\theta)]^{\frac{1}{2}}} \quad . \quad (14)$$

and

$$ql = \int_0^{(\theta_0'-\theta_1)^{\frac{1}{2}}} \frac{2dy}{[\lambda'-(\theta_0'^5-\theta^5)/(\theta_0'-\theta)]^{\frac{1}{2}}}, \quad . \quad (15)$$

where

$$\lambda' = 5\left(\frac{0{\cdot}24\, i'^2}{\gamma_{\text{M}}'m^2n\sigma} + \theta_1{}^4 + \frac{\text{R}}{\sigma}\right). \quad . \quad . \quad . \quad . \quad . \quad (16)$$

5. *General Method of Determination of Mean $\delta\theta$.*

We have in equations (12) and (13)

$$x = f(\lambda, \theta, \theta_0)$$

and

$$l = f(\lambda, \theta_1, \theta_0),$$

so that

$$\lambda = f(\theta_1, l, \theta_0)$$

and is determinate for tapes of fixed length when we have chosen the temperatures at the middle and ends.

Also,

$$\theta_0 = \phi(l, \lambda, \theta_1).$$

Therefore

$$x = f(\phi, \lambda, \theta)$$

and

$$\theta = \text{F}(x, l, \lambda). \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Since λ is determinate, the temperature at any point x can be found.

When external radiation changes the central temperature to θ_0', the corresponding change in λ is to λ', and

$$\theta_0' = \psi(l, \lambda', \theta_1),$$

while

$$\lambda' = f(\theta_1, l, \theta_0').$$

Since θ_0' is arbitrary, λ' is determinate.

Differentiating equation (17),

$$\delta\theta = \frac{\partial F}{\partial\lambda}.\delta\lambda,$$

so that

$$\overline{\delta\theta} = \frac{\delta\lambda}{l}\int_0^l \frac{\partial F(x, l, \lambda)}{\partial\lambda}.dx$$

or

$$\delta\theta = \frac{\delta\lambda}{l}\psi(\lambda, l), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

and is thus a quantity which can be found from the equations of the steady state.

6. *Electrical Resistance Calculation.*

To connect $\overline{\delta\theta}$ with the thickness of tape, we consider the change in resistance on exposure.

Let r_1'=resistance of the tape after exposure. The resistance dr_1, of a strip dx, before exposure, is

$$\frac{1}{\gamma}.\frac{dx}{mn},$$

where

$$\gamma_1 = \gamma[1+\alpha(\theta-\theta_1)]$$

and

$$\gamma_1 = \text{the value of } \gamma \text{ for } \theta=\theta_1.$$

Thus,

$$dr_1 = \frac{1+\alpha(\theta-\theta_1)}{\gamma_1 mn}.dx$$

and

$$r_1 = 2\int_0^l \frac{1+\alpha(\theta-\theta_1)}{\gamma_1 mn}.dx. \quad . \quad . \quad . \qquad (19)$$

Then

$$r_1' = \int_0 \frac{1+\alpha(\theta'-\theta_1)}{\gamma_1 mn}.dx. \quad . \quad . \quad . \qquad (20)$$

Therefore

$$\delta r_1 = 2\int_0^l \frac{\alpha.\delta\theta}{\gamma_1 mn}.dx$$

$$= (2\alpha/\gamma_1 mn).\overline{\delta\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

which gives the mean rise in temperature in terms of the increment in resistance, and the thickness of the tape.

7. *Measure of the Galvanometer Deflexion.*

The best galvanometer resistance g, satisfying the fundamental equation (2), is given by the well-known formula

$$\frac{1}{g}=\frac{1}{r_1+r_3}+\frac{1}{r_2+r_4} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Also we have assumed (paragraph 2) that

$$C_g = f(r_1),$$

which $=0$, in the balance.

Thus

$$\delta C_g = f'(r_1) . \delta r_1$$
$$= (2\alpha/\gamma_1 mn) . \overline{\delta\theta} . f'(r_1)$$

by equation (21).

Using the value of g (constant) determined by equation (22), and differentiating

$$z = \kappa . g^{\frac{1}{2}} . C_g,$$

then

$$\delta z = \kappa . g^{\frac{1}{2}} . (\delta C_g)$$

or

$$\delta z = \kappa . g^{\frac{1}{2}} . (2\alpha/\gamma_1 mn) . \overline{\delta\theta} . f'(r_1) \quad . \quad . \quad . \quad . \quad (23)$$

Equation (23) gives us a measure of the galvanometer deflexion on exposure to radiation. In assuming $C_g=f(r_1)$, we neglect the increment of current through the concealed tape when the resistance r_1 changes to r_1'. Whether or not this assumption can be justified will be more apparent when the method is applied to particular thicknesses of tape.

8. *Balancing Coils.*

We have placed no restrictions upon the relative magnitudes of the resistances in the bridge. In order that the two tapes may be under conditions as similar as possible, it will be assumed that they have equal dimensions, and so equal resistances, before exposure. Then the balancing coils, r_3, r_4, will have equal resistances, and equal currents, ι, $(=\frac{1}{2}C)$ will flow through each tape. Also, by this choice, no current will flow through the galvanometer before exposure, and in consequence δz will in all cases be measured from the same zero.

9. *Application of General Method.*

By means of equation (23) we are attempting to measure the galvanometer deflexion δz, when a tape of known dimensions is exposed to radiant energy. The integration of equations (3) and (7) has for its object the determination of $\overline{\delta\theta}$ over the length of the tape, and by means of the integrals given in equations (12) to (15) this factor can be found. For, if in equations (12) and (13) we write L for

$$2\left[\lambda-\frac{\theta_0^5-\theta^5}{\theta_0-\theta}\right]^{-\frac{1}{2}}$$

and choose any particular value for λ, say λ_p, then for any value of θ, between θ_1 and θ_0, L is determinate. The area under the curve obtained by plotting corresponding values of θ and L will, by equation (13), be equal to ql or $(2\sigma/5kn)^{\frac{1}{2}}.l$, and for a given l, this will fix the value of n, corresponding to the value λ_p, to satisfy equation (13).

If, in addition, we find the ordinate up to which the area under the curve is equal to qx, $(x<l)$, we have determined the upper limit in the integral of equation (12). This gives the value of θ at the point x. Taking a series of values of x and θ, we shall know the temperature distribution over the tape of known thickness, when the temperature at the ends is θ_1 and the central temperature θ_0.

10. When the radiant energy of amount R per unit area falls on the tape we require to solve equations (15) and (14) in the same way as equations (13) and (12). The new central temperature being θ_0' (an arbitrary value), write L′ for

$$2\left[\lambda'-\frac{\theta_0'^5-\theta^5}{\theta_0'-\theta}\right]^{-\frac{1}{2}}.$$

If we give λ' values in the neighbourhood of λ_p, for each value of λ' we shall have a series of values of L′, corresponding to values of θ, for θ between θ_1 and θ_0'. For each value of λ' we can construct a curve connecting θ and L′. The area under each curve is determinate, and by interpolation we can find that value of λ', say λ_p', under which curve the area is equal to ql. We shall arrive in this manner at a solution of equation (15) if λ' be regarded as the unknown.

From the λ_p' curve, as for the λ_p curve, we find the value of θ at the point x, and so the new temperature distribution when the central temperature becomes θ_0'.

The two distributions of temperature determine $\delta\theta$ at the point x, on exposure to radiation, and so $\overline{\delta\theta}$ over the length of the tape. The four equations (12) to (15) are sufficient to determine, for any particular thickness of tape, the mean increment of temperature over the tape when it is exposed to radiant energy.

11. The remaining factors on the right-hand side of equation (23) are readily found. The mean temperatures over the tape, before and after exposure, are given by the curves for λ_p and λ_p' respectively. These temperatures determine γ_M and γ_M', and also, by means of equations (19) and (20), the resistances r_1, $(=r_2)$ and r_1'. Also the resistances r_3 and r_4 are arbitrary, so that equation (22) gives the value of g. The fraction $2a/\gamma_1 mn$ is readily calculated, and the remaining factor $f'(r_1)$ is obtained from the value of C_g. For we have assumed that $C_g=f(r_1)$, so that by differentiating this expression for C_g, and using the values of r_1, r_2, r_3, r_4, proper to the particular thickness of tape, $f'(r_1)$ is determined. R is given by equation (16), and finally, equation (23) gives δz.

12. For each value of n there will be given, by the method outlined, corresponding values of δz and R. It will be shown that, for values of θ_0' between 350° A. and 351° A., δz is proportional to R, when n is constant: so that, for each value of n, δz will be known for a constant R.

Corresponding values of n and δz, for R constant, may then be plotted, and from this curve we expect to find that value of n which makes δz a maximum. In other words, we expect to find a solution of the fundamental equation (1) when throughout the calculations we observe the condition expressed by equation (2).

13. δz *is proportional to* R *when* n *is constant.*

The general method outlined in paragraphs 9, 10, 11 was applied to a tape of thickness 40×10^{-5} cm., of length 1·6 cm., and width 0·01 cm. Four cases were considered, and θ_0' had values between 350° A. and 351° A., while in every case $\theta_1=290°$ A., $\theta_0=350°$ A. The results of these calculations are set out in Table I.

The final column in Table I. shows that within the limits for θ_0' which have been stated, δz may be assumed to vary as R for any particular thickness of the bolometer tape.

14. *Results of Calculations for Various Thicknesses of Tape.*

The general method of calculation was also applied to nine thicknesses of tape varying from $2{\cdot}423\times10^{-5}$ cm. to $583{\cdot}8\times10^{-5}$ cm., and in all cases the following values were used:—$\theta_0=350°$ A., $\theta_0'=351°$ A., $\theta_1=290°$ A., $m=0{\cdot}01$ cm., $2l=1{\cdot}6$ cm. The details of the calculations are not given here, but the principal results obtained from them are set out in Table II., where the final column shows the galvanometer deflexion, δz, following exposure to unit radiation per unit area of the bolometer tape.

TABLE I.

θ_0'.	$\delta z\times10^5$.	$R\times10^5$.	$\delta z/R$.
351	3·815	38·843	0·0982
350·75	2·855	28·991	0·0985
350·50	1·940	19·233	0·1009
350·25	0·972	9·703	0·1002

TABLE II.

$n\times10^5$.	$R\times10^5$.	$\delta z\times10^5$.	$\delta z/R$.
583·8	307·14	11·547	·0376
284·5	160·52	8·239	·0513
156·1	95·28	6·309	·0662
83·3	59·20	4·916	·0831
40·0	38·84	3·815	·0982
13·67	25·86	2·843	·1099
7·161	23·725	2·517	·1061
3·878	23·07	2·130	·0923
2·423	22·89	1·852	·0809

In fig. 1, $n\times10^5$ has been plotted against $\delta z/R$ for values in the neighbourhood of the maximum indicated by the last column in Table II. From the curve we find that δz is a maximum when $n=12\times10^{-5}$ cm.

In view of the graphical method which has been used throughout, the consequent necessity to approximate, and the assumptions which have been made, the result may be more convincing if stated thus :—

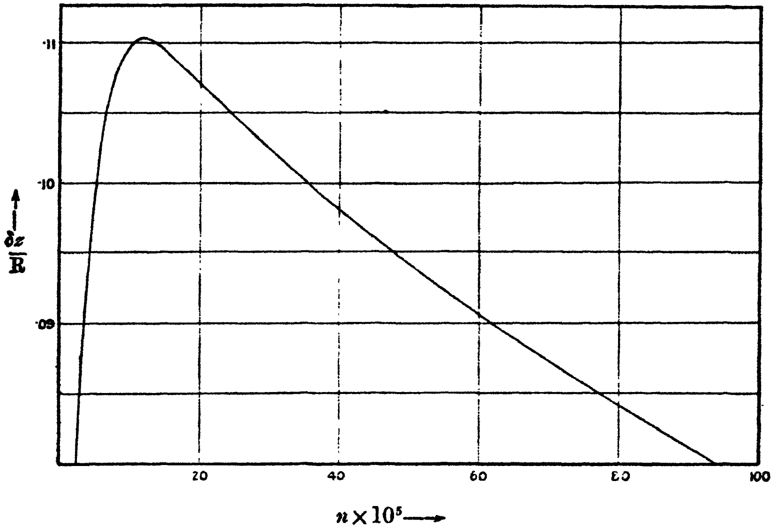
The required solution of equation (1) *is a value of n lying between* $11{\cdot}5 \times 10^{-5}$ cm. *and* $12{\cdot}5 \times 10^{-5}$ cm.

15. *Examination of two Assumptions in the General Method.*

(a) *Resistance variation in concealed tape.*

In paragraph 7 we assumed the resistance r_3 to be constant. When the current i in the exposed tape becomes i' (para. 3, b),

Fig. 1.



Graphical Relation between "$\delta z/R$" and "$n \times 10^5$" to indicate the value of "n" for a maximum "δz."

and the resistance changes to r_1', then $i' < i$. The current in the concealed tape will be increased from i to $C - i'$. The mean temperature of this tape will be increased, and $r_3' > r_3$, if r_3' denote the resistance of r_3 after r_1 has been exposed.

The case where $n = 40 \times 10^{-5}$ cm. was considered in detail, and it was found that the maximum error in the value of r_3 was 0·07 per cent. The errors in $f'(r_1)$ and $g^{\frac{1}{2}}$, factors in the determination of δz by equation (23), were, respectively, less than 0·14 per cent. and 0·15 per cent., and the maximum error in δz less than 3 in 1000. It was not considered that these errors were sufficient to destroy confidence in the result given in paragraph 14.

(b) *Modification for γ variable.*

Equation (3) was integrated when γ had the value determined by

$$\gamma_1 = \gamma[1+\alpha(\theta-\theta_1)]$$

and

$$\gamma_1 = \text{the value of } \gamma \text{ for } \theta = \theta_1.$$

Corresponding to equation (12), we find

$$qx = \int_0^{(\theta_0-\theta)^{\frac{1}{2}}} \frac{2dy}{\left[5\theta_1{}^4+\mu\{2+\alpha(\theta_0-\theta_1)\}+\mu\alpha(\theta-\theta_1)-(\theta_0{}^5-\theta^5)/(\theta_0-\theta)\right]^{\frac{1}{2}}}, \quad (24)$$

where

$$\mu = \frac{5}{2}\left(\frac{0{\cdot}24\, i^2}{\gamma_1 m^2 n\sigma}\right), \quad \text{and } q \text{ as before.}$$

Also we find equations similar to equation (24) corresponding to equations (13), (14), (15).

TABLE III.

	i.	i'.	r_1.	r_1'.	$\overline{\delta\theta}$.	$g^{\frac{1}{2}}$.	$f'(r_1)\times 10^5$.	$\delta z\times 10^5$.
γ constant	0·016455	0·016445	5·368	5·380	0·70	3·114	76·6	3·815
γ variable.........	0·016045	0·016035	5·364	5·376	0·68	3·113	75	3·626

These equations were applied to the case of $n=40\times 10^{-5}$ cm., and a comparison is made of values obtained by this method and the previous method (γ constant) in Table III.

Using the method of γ constant, the tabulated quantities are in excess of their true values. We may reasonably infer that this would be true whatever value of n were chosen. Now we do not seek so much to establish the absolute value of δz for a set of values for n as to obtain a comparative set of values of δz. This is what has been done, and we may conclude that no serious error has been introduced in the result given in paragraph 14 by using γ constant as opposed to γ variable.

16. *Summary.*

In this paper an attempt has been made to find, for bolometer tapes of fixed length and width, what thickness of tape would be best to use in measurements of solar radiation. The bolometer tapes form two arms of a Wheatstone's bridge; the ends of the tapes are supposed to be at a constant temperature, 290° A., and the tapes are supposed heated to a central temperature, 350° A., by an electric current. One tape is exposed to solar radiation and the other tape is shielded from the radiation. The balance in the bridge is destroyed, and a sensitive galvanometer shows a deflexion. This deflexion, for a given amount of incident radiation per unit area of tape, is made a measure of the sensitiveness of the bolometric apparatus for various thicknesses of tape. We wish to investigate what thickness of tape would give a maximum galvanometer deflexion.

Nine different thicknesses of tape were examined, and from the results obtained we conclude:

1. That the best tape to use is one whose thickness is between $11{\cdot}5\times10^{-5}$ cm. and $12{\cdot}5\times10^{-5}$ cm.
2. That where incident radiation raises the temperature at the middle of the exposed tape by 1° C. or less, then, for that particular tape, the deflexion of the galvanometer is proportional to the intensity of the radiation.

The best thickness as here determined is considerably smaller than that in use at the Smithsonian Observatory.

I wish to acknowledge with thanks the assistance I received from Prof. S. Chapman, F.R.S., who suggested the foregoing investigation, and showed me the possibility of using a graphical method for the solution of equations (4) and (8). I wish to offer my thanks also to Prof. E. A. Milne, F.R.S., to whom I am deeply indebted for many suggestions and helpful criticism at numerous stages, as well as for his kindness in reading through the paper and advising important alterations previous to its appearing in the present form.

Newport, Mon.,
18th Jan., 1929.

CXIX. *The Lattice Energy of* LiH *and the Normal Potential of* H$^-$. *By* R. S. BRADLEY [*].

1. *The Lattice Energy of* LiH.

THE crystal structure of LiH was studied by Bijovet ⁽¹⁾. He found for the internuclear distance 2·01 A.U. This agrees with the value 2·03 A.U. calculated from the moment of inertia of LiH, 6 10^{-40} gm. cm.^{2}, obtained by Watson ⁽²⁾ from band spectra. Bijovet was unable to decide whether the lattice was ionic or atomic. In this paper the lattice energy will be calculated on the former assumption.

LiH is similar to KCl in that both ions have the same type of electron sheath. The repulsive exponent n for He is determined uniquely as 14·33 and the force constant λ_n as 2·35 10^{-115} ⁽³⁾. It will be assumed that n for the helium-like ions Li^+ and H^- has not been changed by deformation. The exponent is higher than that usually encountered in crystals and determined from the compressibility. Rashevsky ⁽⁴⁾, however, has pointed out that the latter method assumes a perfect crystal, whereas the real crystal contains cracks.

The force constants for LiH may be calculated by a modification of the method of Lennard-Jones :

$$\lambda_{Li^+} = \left(\frac{\rho_{Li^+}}{\rho_{He}}\right)^{n-1}\lambda_n, \quad \lambda_{H^-} = \left(\frac{\rho_{H^-}}{\rho_{He}}\right)^{n-1}\lambda_n,$$

where ρ is the atomic or ionic radius, taking $\rho_{Li^+} = \cdot 78$ ⁽⁵⁾, $\rho_{He} = \cdot 945$ ⁽⁶⁾. The published values for ρ_{H^-} are discordant. The value taken, 1·40 A.U., lies on the line obtained by plotting ionic radius against nuclear charge for the series He, Li^+, Be^{2+} (·34 A.U.), all of which have He-like sheaths, and agree roughly with Pauling's ⁽⁷⁾ computation 1·51 A.U. A similar linear relation holds for Ne-like sheaths, etc.

The force constants are then

$$\lambda_{Li^+Li^+} = 1{\cdot}820\ 10^{-116}, \quad \lambda_{H^-H^-} = 4{\cdot}427\ 10^{-113},$$

$$\lambda_{Li^+H^-} = 1{\cdot}445\ 10^{-114}.$$

The lattice energy

$$-U = \frac{1}{2}\frac{N\phi}{J}, \quad J = 4{\cdot}2\ 10^7, \quad N = 6{\cdot}06\ 10^{23},$$

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[*] Communicated by the Author.

where

$$\phi = \frac{e^2\, 3\cdot495}{a} - \frac{2\lambda_{\mathrm{Li^+H^-}}A'_{(n-1)} - (\lambda_{\mathrm{Li^+Li^+}} + \lambda_{\mathrm{H^-H^-}})A''_{(n-1)}}{(n-1)a^{n-1}},$$

a is the internuclear distance, e the electronic charge, n the repulsive exponent, and A′ and A″ numbers obtained by interpolation from Lennard-Jones's tables as

$$A'_{n-1} = 6\cdot006, \quad A''_{n-1} = \cdot1204.$$

The van der Waals's attractive force has been neglected.

Inserting these values we get $-U = 230\cdot5$ k.cal. The calculation may be checked by obtaining a value for a. For minimum potential energy we get

$$a^{n-2} = \frac{(\lambda_{\mathrm{Li^+Li^+}} + \lambda_{\mathrm{H^-H^-}})A''_{(n-1)} + 2A'_{(n-1)}\lambda_{\mathrm{Li^+H^-}}}{3\cdot495\, e^2},$$

$a = 2\cdot18$ A.U., as compared with the experimental value 2·01 A.U.

2. *Comparison with the Value calculated from a Cycle.*

U may be calculated from the cycle

$$\begin{tikzcd}
\mathrm{Li\ (solid)} + \tfrac{1}{2}\mathrm{H_2} \arrow[r] \arrow[d] & \mathrm{LiH\ (solid)}, \arrow[d] \\
\mathrm{Li\ (gas)} + \tfrac{1}{2}\mathrm{H_2} \arrow[r] & \mathrm{Li^+} + \mathrm{H^-}.
\end{tikzcd}$$

The energy changes are :

Li (liquid) ⟶ Li gas	−48·0 k.cal.[8]
Li (solid) ⟶ Li (liquid)	−·23 k.cal.
$H_2 \longrightarrow 2H$	−100·1 k.cal.[9]
Li (solid) + ½ H_2 ⟶ LiH (solid)	+21·6 k.cal.
$Li \longrightarrow Li^+ + e$	+123·5 k.cal.[10]
$H + e \longrightarrow H^-$	−1·85 k.cal.[11]

Hence $U = -245\cdot2$ k.cal. The discrepancy between this value and the theoretical is not large, and is due to the uncertainty of ρ_{H^-} and of n in the crystal.

3. *The Normal Potential of* H^-.

Owing to the difference between the lattice energies of LiH and LiF (-245 and -254[12] k.cal. respectively), giving a notable difference in the heat of solution, it is not permissible to use the method of Proskurnin and Kasarnowsky[13] to determine the normal potential of H^-. Instead it will be assumed that the heat of hydration of $H^+ + H^-$ is the same as that of $H^+ + F^-$. This requires a similar identity for ionic entropies[14].

The cell $H^+aq + H^-aq \longrightarrow H_2$ is an interesting oxidation-reduction system, with the half elements

$$H^- \longrightarrow \tfrac{1}{2} H_2 + e, \quad \tfrac{1}{2} H_2 \longrightarrow H^+ + e.$$

The heat of hydration of $H^+ + F^-$ to dilute solution may be obtained from the cycle

$$\begin{tikzcd} HF \arrow[r] \arrow[d] & H^+ + F^- \arrow[d, dash] \\ H^+ aq + F^- aq & {} \arrow[l] \end{tikzcd}$$

The energy changes are:

$$HF \longrightarrow H^+ + F^- \; \ldots\ldots\ldots \; -373 \text{ k.cal.}^{(15)}.$$

$$HF \longrightarrow H^+ aq + F^- aq \ldots \; +11{\cdot}6 \text{ k.cal.}^{(16)}.$$

ΔH for the cell reaction is then calculated from the cycle

$$\begin{tikzcd} H_2 \arrow[r] \arrow[d, dash] & H^+ + H^- \arrow[d] \\ {} \arrow[r] & H^+ aq + H^- aq \end{tikzcd}$$

to be -29 k.cal. Latimer gives $S_0(F^-) = -5$[17]. $S_0(H_2)$ is 29·4. Hence

$$\Delta F_0 = \Delta H - T\Delta S_0,$$
$$= -39{\cdot}3 \text{ k.cal. at room temperatures.}$$

E_0 for the half element $\tfrac{1}{2} H_2 \longrightarrow H^+ + e$ is zero, and hence E_0 for the half element $H^- \longrightarrow \tfrac{1}{2} H_2 + e$ is $-1{\cdot}70$ volts. This is the normal potential of H^-. We may use it to calculate equilibrium concentrations of H^-aq. These will clearly be highest when the concentration of OH^-aq is a maximum.

For the reaction $H^+ aq + H^- aq \longrightarrow H_2$,

$$\mathrm{RT} \log_e \frac{P(H_2)}{a(H^+)a(H^-)} = -\Delta F_0 = 39{\cdot}3 \text{ k.cal.},$$

where $P(H_2)$ is the pressure of H_2, and $a(H^+)$ and $a(H^-)$ are activities.

Hence for $P(H_2) = 1$,

$$\log_{10} a(H^+)a(H^-) = -28{\cdot}6.$$

Thus, when the p.h. is about 14 the concentration of H^- is still as low as $10^{-14}-10^{-15}$. It may be increased by using some other oxidation-reduction system, such as

$$Fe^{2+} \longrightarrow Fe^{3+} + e.$$

For the reaction $Fe^{3+} + H^- \longrightarrow Fe^{2+} + \frac{1}{2} H_2$,

$$\mathrm{RT} \log_e \frac{a(Fe^{2+})}{a(H^-)a(Fe^{3+})} = 2{\cdot}41 \text{ volt . faradays},$$

when $P(H_2) = 1$.

Hence $$\log_{10} a(H^-) = \log_{10} \frac{a(Fe^{2+})}{a(Fe^{3+})} - 41{\cdot}6.$$

For $a(H^-)$ to be 1, the ratio $\frac{a(Fe^{2+})}{a(Fe^{3+})}$ would thus have to be $10^{41{\cdot}6}$.

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The University, Leeds,
25 March, 1929.

CXX. *The Electric Arc in Mixed Gases.* By F. H. Newman, *D.Sc., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter*[*].

[Plate XXIII.]

1. *Introduction.*

It has been shown by many experimenters that profound modifications are sometimes observed in the spectrum of a substance when impurities are present, and although most of the investigations have been made on gases in a discharge-tube the effect is also found when the arc is used. Sometimes the spectrum of the impurities is brighter than that of the gas present in bulk, and this is particularly manifest with impurities in the inert gases. Rayleigh[†] has found that the spectrum of the nitrogen after-glow is modified by the presence of the inactive gases, the effect depending upon the nature of the inactive gas used. Merton and Barratt[‡], employing tubes containing hydrogen and helium at different relative pressures, observed that when the helium was at a comparatively high pressure the lines of both helium and hydrogen appeared with uniform intensity throughout the capillary with an uncondensed discharge, but on placing a condenser and a spark-gap in the electrical circuit the hydrogen lines became much weaker in the centre of the capillary. On the other hand, the mercury lines were intensified with the condenser in the circuit, and they behaved in exactly the opposite manner to the hydrogen lines. Johnson and Cameron[§] noted a more striking difference in the spectrum of carbon in the presence of argon and helium, for whereas in the latter gas the "comet tail" spectrum and the new line spectrum appear with uncondensed and condensed discharges, respectively, neither of these spectra could be observed under any conditions of excitement when argon was substituted for helium, although the new triplet series of bands could be developed in either gas.

The lines of the Balmer's series are strongly enhanced relatively to the secondary spectrum by very small traces of impurities, and it seems remarkable that any profound influence on the spectrum of a gas can be exerted by impurities which are present in such small quantities that their presence cannot be detected by any characteristic lines or bands in the spectrum. The difficulty of eliminating such impurities as those which give rise to the carbon bands is familiar to all workers with vacuum tubes, and the relative intensities of the lines and bands due to impurities are enhanced enormously as the pressure increases. In addition, the forms in which the impurities appear are also often unusual. McLennan and Shrum [*], studying the effect of large admixtures of helium or of neon on the spectrum of oxygen, photographed the line λ 5577, which is identical with the auroral green line λ 5577, and attributed it to some hitherto unknown spectrum of oxygen. Although this line is not obtained in mixtures of pure helium and nitrogen, the presence of the helium greatly enhances the negative bands of nitrogen, but it has little effect upon the second positive group. There is no evidence that a trace of oxygen in a tube containing helium at high pressure would alter the spectrum of the latter very considerably, and, moreover, such an effect is not observed with nitrogen. A strong electric field of atomic origin may displace or resolve a band, and thus an increase of pressure will bring the molecules of a substance into sufficient proximity to produce an electric field strong enough to cause ordinary flutings to appear as continuous bands. The helium atoms have a very small electric field, and therefore, with only a trace of oxygen in helium, the atomic electric forces on the oxygen atoms will be relatively small, and the electron groups occurring under these conditions may give some new radiations.

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[*] Communicated by the Author.

[†] Proc. Roy. Soc. A, cii. p. 453 (1923).

[‡] Phil. Trans. A, ccxxii. p. 369 (1922).

[§] Proc. Roy. Soc. A, cvi. p. 195 (1924).

More recently Keys and Home [†] have investigated, spectroscopically, the striated discharge in mixtures of (*a*) nitrogen and hydrogen, (*b*) helium and hydrogen, spectrograms being taken of the light emitted by the negative glow and by the striations, respectively. The electronic energies in the different regions of the discharge are interpreted from these spectra to determine the extent of the ionization in different parts of the tube. Their results indicate that the presence of helium in some way prevents the excitation of H_α and H_β in the negative glow, and enhances these lines in the striations. They suggest that the inert gases cause a redistribution of the electronic energy. Terroux [*] investigated mixtures of argon and hydrogen, and of argon and oxygen, photographing the spectra of the negative glow and of the striated positive column. The change in concentration was found to make little difference in the distribution of electronic energy, and his results seem to indicate that the exciting potentials are correlated with the spectra emitted. Various data suggest, however, that the ionizing potential is not the sole controlling factor in the emission of any particular type of radiation. For example, Keys and Home found the Balmer lines more strongly developed in the striations than in the negative glow, whereas the reverse appears in argon. This, as pointed out by Terroux, may be due to the fact that in argon and hydrogen the ionization potential of argon is slightly less than that of hydrogen, whereas that of helium is one-and-a-half times as great. An electron having a velocity of a little over 15 volts would probably make an elastic collision with a helium atom, and could still ionize a hydrogen atom, but the same electron colliding with an argon atom would ionize the latter and so lose its kinetic energy.

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[*] Proc. Roy. Soc. A, cviii. p. 501 (1925).

[†] Phys. Rev. xxvii. p. 709 (1926).

Compton [†], investigating the production of atomic nitrogen, found that large currents and high helium pressure favour dissociation of nitrogen, by the action of the excited helium atoms on nitrogen, and with low partial pressures of the latter the arc spectrum of this element is emitted. If the nitrogen is present in large proportion the electrons collide inelastically with nitrogen molecules, and thus lose their energy without exciting the helium. It is only when the proportion of gas is extremely small that the electrons attain the energies required for the helium excitation. Thus Compton has calculated that at 20 mm. helium pressure the nitrogen pressure should be less than 0·01 mm., probably considerably less, in order that most of the electron energy should go directly into the helium. On the other hand, the amount of nitrogen must be sufficient to be appreciable.

The author [‡] has already discussed the variations that occur in the intensity of the spectra of alkali-amalgam vapours when the experimental conditions are varied. For example, with sodium amalgam at temperatures above

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[*] Phys. Rev. xxvii. p. 1242 (1926).

[†] Phil. Mag. l. p. 512 (1925).

[‡] Phil. Mag. xlv. p. 18 (1923); xlv. p. 293 (1923).

200° C. the sodium lines are very intense compared with the mercury lines, whereas at temperatures below 100° C. the mercury lines are predominant, and they were consistently brighter than the potassium lines when a potassium-amalgam was excited. These opposite effects with the two alkalis are difficult to explain. The ionization potential of mercury is greater than that for sodium and potassium, and the mercury vapour pressure is higher at all temperatures. It is evident, therefore, that the ionization potential is not the only critical factor in determining the relative intensity of the spectrum lines in gaseous and vapour mixtures. It was found also that the relative brightness of the individual spectra changed considerably as the nature of the electrical discharge varied. If the vapours of mercury and any one of the alkali metals were both present in the discharge-tube, while the partial pressures were maintained constant, the spectrum of the alkali was always well developed with the ordinary type of discharge, but was completely masked by the mercury lines with the condensed discharge. All of the alkali metals have lower resonance and ionization potentials than mercury, so that although the amount of mercury present may be comparatively great yet the electrons during their mean free paths are more likely to acquire the energy necessary for ionization of the alkali atoms. As a result the concentration of the luminous sources may be great enough to exhibit the alkali spectrum. With the condensed discharge, and consequent increase in the electrical energy, a greater proportion of the mercury atoms will be ionized because the colliding electrons will attain higher energy during the mean free paths. The mercury lines become very bright. At the relatively high pressures employed the mean free path has a small value, and it is unlikely that the ionizing energy can be obtained by impact alone; more probably it is acquired chiefly by radiation absorption.

Practically no work on the relative intensity of spectra excited by means of the arc has been done, but the author * has shown that when an arc is passed through hydrogen which has not been dried the Balmer lines are not accompanied by any continuous spectrum, whereas with dry gas the secondary spectrum, together with a continuous spectrum, are both intense. It is evident, therefore, that traces of foreign vapours will affect the arc spectra of gases and

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* Phil. Mag. vi. p. 807 (1928).

vapours, and in most cases the changes produced may be expected to resemble those made by the uncondensed electrical discharge.

2. *Experiments.*

One of the most convenient methods for investigating the arc in various atmospheres is that described by the author *, in which a temporary discharge is sent between two electrodes, a potential difference being applied between one of these electrodes and a third one. This arrangement starts and maintains the arc, and provided that it is not allowed to continue for any length of time, the radiation emitted is that characteristic of the gas, few iron lines appearing. In this way very large currents may be sent through the gas. In the present work, after the tube had been exhausted to 10^{-5} cm. pressure, the gas under examination was admitted in small doses, and thus any required pressure could be obtained. For some experiments the gas was mixed with a little water vapour, while in others it was carefully dried by allowing it to stand over phosphorus pextoxide for several hours. Helium and neon were tested separately, each gas being 98 per cent. pure and containing 2 per cent. of the other gas as an impurity. From the results obtained it was evident that the impurity had little if any effect upon the phenomena occurring, so that the impurity was not removed.

An arc such as described above can be started in hydrogen at low pressure and also in the residual gases remaining in the tube after exhaustion, but great difficulty was experienced in striking the arc in helium and neon atmospheres at all pressures varying from 10^{-3}–1 mm. Even when the arc was started it could not be maintained, but if a small bead of borax was fused on to the cathode this difficulty was eliminated and the arc started and persisted as in hydrogen. The characteristic radiations associated with helium and neon were absent, the core of the arc being brilliant white in colour with a surrounding column of yellow-coloured radiation which, when examined, showed only the D lines. The Balmer lines were present together with the CN bands and many other lines which have not been completely classified. The helium and neon spectra could be detected when the dried gas was used, but even in this case the lines were faint compared with the other lines and bands. If the arc was interrupted, and the potential difference re-applied across the electrodes immediately after the interruption, a blue glow appeared in the vicinity of the cathode, and persisted for a short time. This glow is attributed to the fact that in the immediate neighbourhood of the electrode the potential fall is sufficient to speed up the residual ions so that they attain energy equivalent to the ionization potentials of the gases present. The glow was faint and existed for such a short interval of time that it was not possible to examine it spectroscopically.

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* *Loc. cit.*

The luminous radiation from the arc was photographed through a quartz window by means of a quartz spectrograph, special rapid panchromatic plates being used. An examination of the results obtained with helium which had not been dried showed that the helium lines were very faint, the Balmer lines from hydrogen present as an impurity being much stronger. Mercury lines, especially λ 2537, and the ammonia bands were prominent, but the CN bands, particularly those at λ 3883 and λ 3590, were by far the most intense lines on the plates. The actual percentage of nitrogen, carbon monoxide, carbon dioxide, etc. present in the tube must have been exceedingly small, and when the arc was sent through these residual gases the CN bands did not appear, so that helium and neon cause emission of the bands even when the amounts of nitrogen and carbon compounds present as impurities are very small. A careful examination of the plates did not reveal any of the nitrogen arc lines such as Compton found when helium was mixed with a small percentage of nitrogen. The striking difference between the spectra of the residual gases and of these gases mixed with helium and neon is seen in Pl. XXIII.

When the helium was replaced by neon which had been thoroughly dried, the Balmer lines were relatively faint compared with the neon ones; otherwise there was very little difference. If the arc were allowed to burn for a short interval the electrodes become very hot and the iron lines appeared. These lines, however, had different relative intensities compared with the results obtained with the iron arc in air. In particular it was noted that the group of lines λ 2382–λ 2411 were intense if water-vapour was absent.

The faintness of helium and neon lines in this type of arc is interesting, especially as the ordinary electric discharge through these gases gives the characteristic spectra associated with them. The CN bands which are prominent may be excited thermally at a temperature of 2100° C. and correspond to electronic resonance potential of 3·18 volts. The equilibrium concentration of CN may be expected to increase with temperature and to become a relatively abundant molecular species. Thus in the carbon arc, which has a temperature of about 4000° C., the bands are of great intensity, and in the present type of arc, although it is not at such a high temperature, it has a value sufficiently great to vaporize the iron electrodes after a few seconds, so that conditions are favourable for the formation of CN. Since the low resonance potential indicates a low ionization potential, it appears that the CN is ionized by the colliding electrons of comparatively small energy. Helium possesses minimum excitation states of 19·73 and 20·56 volts, the ionization potential for atoms of this gas being 24·5 volts. To produce the Balmer lines from molecular hydrogen requires 15·5 volts and the negative bands of nitrogen require 17·75 volts, so that at higher gas pressures the chance of electrons acquiring the ionizing energy is least for helium and greatest for CN. The helium atoms increase by elastic collisions the total path of the electrons through the tube and thus increase the chance of collision with a molecule of CN, and it is only when the proportion of nitrogen, hydrogen, carbon dioxide, etc. is extremely small that the electrons attain the energy necessary for excitation of the helium. As the helium gas pressure is increased the amount of nitrogen, etc. must be diminished if most of the electrons are not to lose their energy directly to the nitrogen. Although the actual amount of CN produced by the high temperature of the arc would of necessity be small the percentage ionized should be high, since the probability of two ionized CN molecules colliding would be less than the chances of one meeting with a helium atom. During collisions between helium atoms in the excited state and molecules of CN the excited helium atoms may return to their normal state without radiation, the energy, which would appear as radiation if the atom were to pass spontaneously from a higher stationary state to a lower one, ionizing the CN molecules, and the CN bands accordingly appear.

The cathode potential fall, although not measured in the present arc, is undoubtedly sufficient to ionize any of the gaseous molecules and atoms present, and this cathode fall is reduced by fusing the borax on the electrode. When it is reduced below a value of 120 volts, approximately, it is not sufficient to produce ionization of the molecules and the arc will not start.

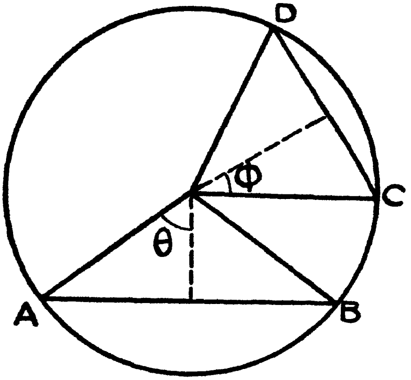
CXXI. *Note on a Geometrical Radiation Problem.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the February issue of the Philosophical Magazine, Prof. E. A. Milne has treated the problem of the radiation reaching one circular disk from another. This problem was one of those treated by J. H. Lambert in his 'Photometria sive de mensura et gradibus luminis, colorum et umbræ' (1760), and the formula is to be found on p. 100 of the original work or on p. 81 of the German translation (Ostwald's 'Klassiker,' Nr. 31).

Fig. 1.



Prof. Milne also refers to the fact that when the disks are of equal radius the radiation reaching one disk from the other is less than that which would reach it from an infinitely large disk, in the ratio $\tan^2\frac{1}{2}\theta$. He states that no simple method of proof of this result has suggested itself. The result is, however, quickly obtained from the well-known principle that a disk, the edge of which forms a circle on a sphere, receives equal amounts of flux from equal areas of the sphere surface irrespective of the positions of those areas[*]. Thus the radiation reaching AB (see fig. 1) from the area CD is less than that reaching it from the whole area BCDA in the ratio of the spherical area cut off by the disk CD to the spherical area BCDA, *i.e.*, in the ratio

$$(1-\cos\phi)/(1+\cos\theta)=(\sin^2\tfrac{1}{2}\phi)/(\cos^2\tfrac{1}{2}\theta).$$

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[*] See, *e.g.*, Phys. Soc. Proc. xxxii. p. 59 (1920).

In the special case when the disks are equal this reduces to Prof. Milne's expression, $\tan^2\frac{1}{2}\theta$. It is to be noted that parallelism of the disks is not necessary. All that is postulated is that the edges of the two disks shall form small circles of the same sphere.

Yours truly,
John W. T. Walsh.

The National Physical Laboratory,
Teddington, Middlesex,
4th April, 1929.

CXXII. *Uniformly Diffused Light through Two Apertures.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In the February issue of the Philosophical Magazine, Dr. A. Gerschun has pointed out that the above problem, solved by Prof. L. F. Richardson [*] as an example of his method of computation by "deferred approach to a limit" [†], has an analytical solution which is, in fact, a special case of the solution of a more general case given in Herman's 'Treatise on Geometrical Optics.' The amount of flux that will go in series through two apertures forming opposite faces of a cube of side l can thus be shown to be equal to

$$0{\cdot}627768\, l^2\mathrm{B},$$

where B is the brightness of the side admitting the flux. It is of interest to notice that, since the total flux admitted by this side is $\pi l^2\mathrm{B}$, the amount reaching each of the four adjacent sides is

$$\tfrac{1}{4}(\pi-0{\cdot}627768)\,l^2\mathrm{B}$$
$$=0{\cdot}628456\, l^2\mathrm{B}.$$

Thus the interesting result is obtained that, to 0·1 per cent., each of the five sides receives $\frac{1}{5}\pi l^2\mathrm{B}$.

It is, perhaps, of interest to point out that the general problem is of considerable practical importance in illuminating engineering for calculating the amount of light which reaches the walls of a rectangular light-shaft in a building, assuming the shaft to be open at the upper end to a sky of uniform brightness. If reflexions from the walls be neglected, it is clear that the flux reaching an elementary strip of the walls of height dc, situated at a distance c below the top of a shaft of sides a, b, is equal to the first differential with respect to c of the expression given by Herman, viz.,

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[*] Phil. Mag. vi. p. 1019 (Nov. 1928).

[†] Phil. Trans. Roy. Soc. A, ccxxvi. p. 299.

$$\mathrm{B}\left[c^2\log\frac{(c^2+a^2)(c^2+b^2)}{c^2(c^2+a^2+b^2)}+2a(c^2+b^2)^{\frac{1}{2}}\tan^{-1}\frac{a}{(c^2+b^2)^{\frac{1}{2}}}\right.$$
$$\left.-2ac\tan^{-1}\frac{a}{c}+2b(c^2+a^2)^{\frac{1}{2}}\tan^{-1}\frac{b}{(c^2+a^2)^{\frac{1}{2}}}-2bc\tan^{-1}\frac{b}{c}\right].$$

Yours very truly,
JOHN W. T. WALSH.

The National Physical Laboratory,
Teddington, Middlesex,
4th April, 1929.

CXXIII. *Frequency Variations of the Triode Oscillator.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the January number of the Philosophical Magazine, Lieut.-Col. K. E. Edgeworth again attempts to prove that his paper read before the Institute of Electrical Engineers (Wireless Section) on the 6th of January, 1926, is in many respects similar to my paper under the above title in the Philosophical Magazine for November 1927; and he repeats that, "So far as they cover the same ground, the experimental results appear to be in agreement and the explanations offered are substantially the same." In his latest note Edgeworth seeks to prove that my equation,

$$p^2=\frac{1}{\mathrm{L}_1\mathrm{C}_1+k_1k_2(\mathrm{L}_1\mathrm{L}_2-\mathrm{M}^2)}, \quad . \quad . \quad . \quad . \quad (1)$$

which is fundamental to the work, is already contained in his paper in the form:

$$f=\frac{1}{2\pi\sqrt{\mathrm{L}_1\mathrm{C}_1}}\left\{1+\frac{1}{2\mathrm{A}}\left(\mathrm{R}_1-\frac{\mathrm{R}_2\mathrm{C}_2}{\mathrm{C}_1}-\frac{\mathrm{R}_1\mathrm{R}_2\mathrm{C}_2}{2\mathrm{L}_1}\right)\right\}. \quad (2)$$

Incidentally, it may be mentioned that this latter equation appears not in Edgeworth's paper, but at the end of his reply to the discussion, and that the method by which it is derived is not indicated. Coupling this equation (2) with a third equation,

$$R_2C_2 = R_4C_2 + \frac{L_2\sigma}{G}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which he states to be given in the body of his paper immediately after equation (18), Edgeworth derives the equation:

$$f = \frac{1}{2\pi\sqrt{L_1C_1}}\left\{1 - \frac{\sigma L_2}{2AC_1G}\right\}. \quad . \quad . \quad . \quad (4)$$

He now makes the assumption that in my equation (1), $k_1k_3\,(L_1L_2 - M^2)$ is small compared with L_1C_1, and then shows that equations (1) and (4) are identical. Edgeworth then states that "The identity of these two equations provides a formal proof that the frequency variation investigated by Martyn is the same as the frequency variation of the first type discussed in my paper. . . . Most of the points discussed in Martyn's first paper . . . can be derived from any of the above equations with equal facility." How completely fallacious is this point of view the following considerations prove.

(1) The frequency variations examined in my paper, both experimentally and theoretically, *are extremely large and extend over several octaves.* Hence Edgeworth's equation, which, as he says himself, is only valid for small variations of frequency, cannot possibly be made to apply thereto. It is absolutely impermissible for Edgeworth to take my equation (1), assume that $k_1k_3(L_1L_2 - M^2)$ is small compared with L_1C_1, and then show that my equation can be transformed into his equation (4) because $k_1k_3(L_1L_2 - M^2)$ is usually several times greater than L_1C_1 in my work. Hence Edgeworth has really proved that my equation (1), which was derived to explain large frequency variations, can also explain small variations of frequency such as were obtained by Edgeworth—a fact which is, *ab initio*, obvious. But he has completely failed to prove his contention that his own equation (4) can explain the large frequency variations which I obtained.

(2) Edgeworth uses the equation (3) in "proving" the identity of equations (1) and (4) above. This equation is stated to appear in his paper after equation (18). On consulting his original paper at the place mentioned, I find the following equation:

$$R_2C_2 = R_4C_2 + \frac{L_2}{G}.$$

Where the σ has come from in equation (3) is a mystery, but certainly without its appearance not even an attempt at "proof" of the identity of our equations could be made.

There is no doubt that for frequency variations of any importance equation (1) supplies the complete explanation, and that the causes of variation theoretically considered by Edgeworth are of minor importance, as pointed out in my last note.

Yours faithfully,
D. F. Martyn, Ph.D.

CXXIV. *Notices respecting New Books.*

An Introduction to Crystal Analysis. By Sir William Bragg, K.B.E., D.Sc., F.R.S. [Pp. vii+168, with 105 figures.] (London: G. Bell and Sons. 1928. Price 12*s.* net.)

The Structure of an Organic Crystal. By Sir William Bragg, K.B.E., D.Sc., F.R.S. [Pp. 32, with 10 figures.] (London: Longmans, Green and Co. 1928. Price 1*s.* 6*d.* net.)

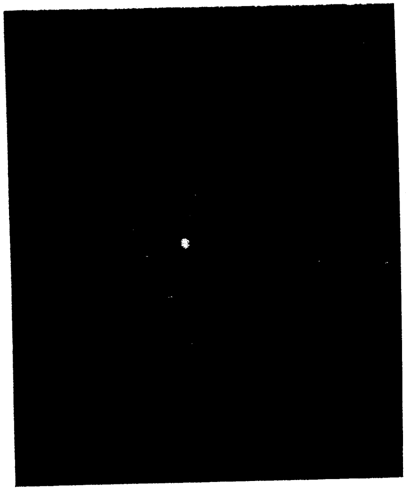
The application of X-rays to the study of crystals has given valuable information about the structure of crystals, both inorganic and organic, and has proved of great assistance to the chemist, the metallurgist, and the crystallographer. In the first of the above volumes, an excellent account is given of the principles underlying the methods of crystal analysis, of the various experimental arrangements employed, and of some of the results obtained. One chapter is devoted to the various types of space groups or crystal arrangements. The examples include simple inorganic crystals of the atomic type, such as the diamond, and of the ionic type, such as calcium fluoride; somewhat more complex crystals such as calcite; complex crystals such as the alums and various organic substances; and metal crystals. The volume throughout is characterized by the author's gift of clear, simple exposition, and forms an excellent introduction to the new subject.

The second volume contains the Fison Memorial Lecture, 1928, delivered at Guy's Hospital Medical School. It deals with the structure of organic crystals as deduced from X-ray analysis and the bearing of the results upon the structure arrived at by chemists from purely chemical considerations.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

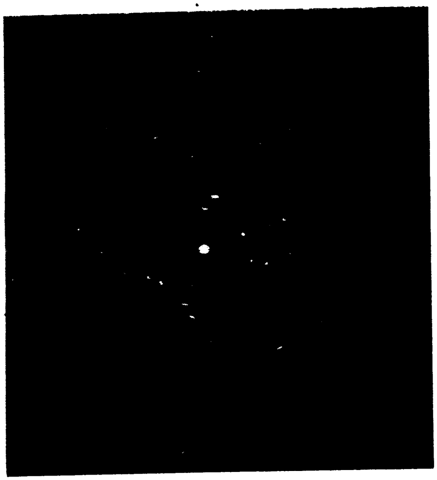
Cox & Backhurst.

No. 4.



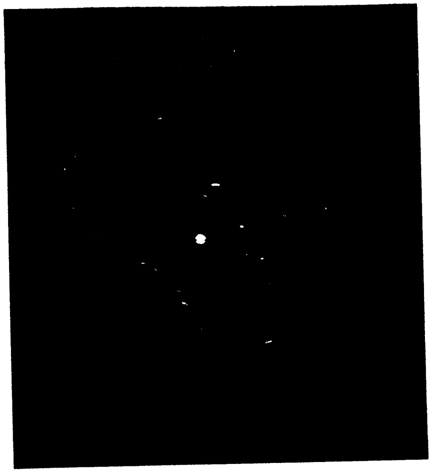
2 tons/sq. in.

No. 20.



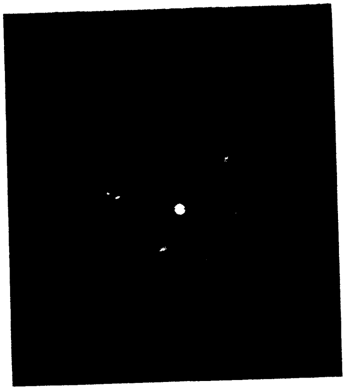
80 tons/sq. in.

No. 21.



88 tons sq. in.

No 22



97 tons sq. in.

Laue Diagrams of Tungsten Crystal W.C. 1.

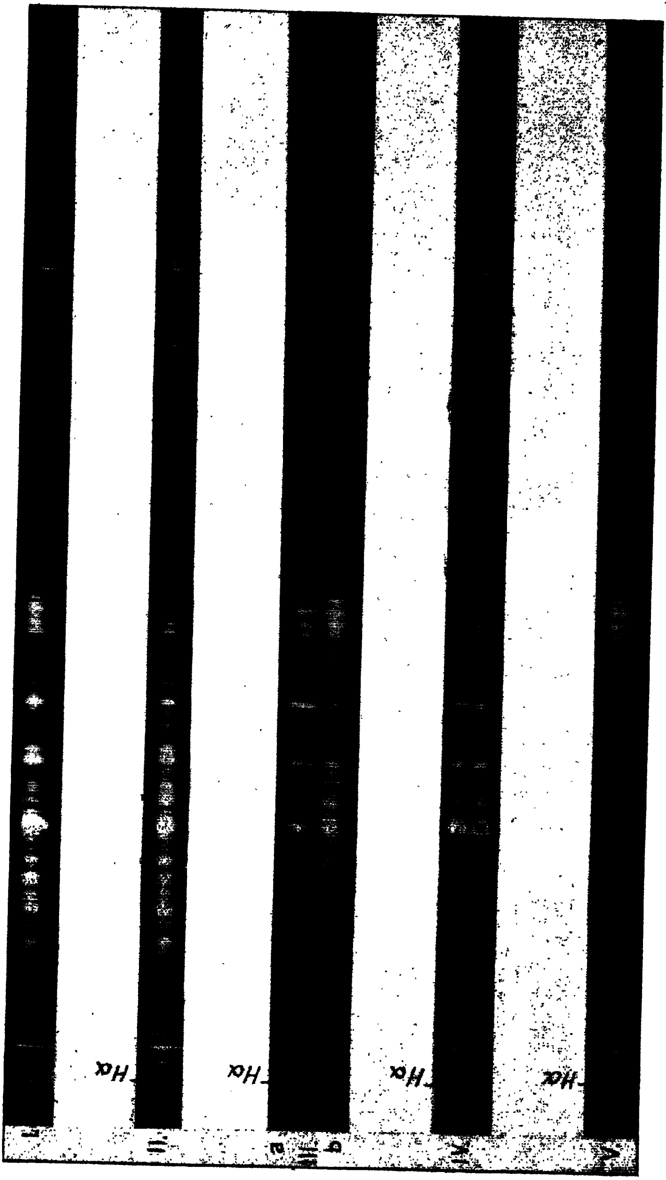
No. 23.

104 tons sq. in.

No. 24.

1 ton/sq. in.

NEWMAN. Phil. Mag. Ser. 7, Vol. 7, Pl. XXIII.



SPECTRA OF ARC THROUGH MIXED GASES.

I. Helium. Water-vapour present. II. Helium. Dry.
III. (a) Neon. Water-vapour present; (b) Neon with Iron lines.
IV. Neon. Dry. V. Residual gas spectrum.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

JUNE 1929.

CXXV. *The Constitution and Density of Particles in Precipitated Smokes.* *By* H. P. Walmsley, *M.Sc.**.

THIS paper describes the results obtained from X-ray data for particles in electrically precipitated smokes which were produced by the volatilization of metals from an electric arc in air. The precipitates form bulky flocculent powders. The best-known example, although not usually prepared in this way, is the deposit from a zinc oxide smoke—the so-called "philosophers' wool." The colour, appearance, and general properties of many of the precipitates have been described by Kohlschütter and Tüscher (1), who incidentally give values of the density in bulk of some of them. The results come out much less than the normal densities of the material of which they are composed, *e.g.*, values of 0·83, 0·56, 0·46 were obtained for the smoke of lead monoxide, the normal density of which is 9·6.

Indirect measurements of the density of individual particles actually in suspension in a smoke have been made by various observers with similar results. Meyer and Gerlach (2) measured the rate of fall of a given particle at various gas pressures, and found that they could only make their results self-consistent by assuming a density of 11·56 for particles from platinum, the normal density of which is 24·1. Bär (3), using the same method, obtained similar results and concluded that the particles were not homogeneous but possessed either a sponge-like structure or an irregular non-spherical shape. The validity of the deduction was disputed on theoretical grounds by Sexl(4). Patterson and Whytlaw-Gray(5) used the method devised by Ehrenhaft and Millikan for the determination of the electronic charge, to measure the densities of individual particles in smokes from various substances dispersed in air. As an example, particles from silver ($\rho=10{\cdot}5$) gave values ranging from 4·22 to 0·64. Here again it was considered that the particles on which measurements were made were agglomerates of smaller units loosely held together, and that the values obtained were averages for heterogeneous aggregates. With the necessary changes, the objections of Sexl may be directed equally against these results.

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* Communicated by Prof. W. L. Bragg, F.R.S.

The question of the constitution of a smoke particle involves two distinct problems—the nature of the ultimate units from which the particle is built and the manner in which the units are assembled. The present work is an attempt to solve the first only of these problems, but it gives a hint as to the probable solution of the other. We may anticipate the results by saying that the ultimate units prove to be crystalline particles of the normal density of the material of which they are composed. The general conclusions of Bär and Patterson and Whytlaw-Gray are therefore supported. It seems probable that the particles they examined in many cases were really crystal aggregates. The observations of Kohlschütter and Tüscher are easily explained. Briefly, the relation between philosophers' wool and zincite—the crystallized form of zinc oxide—is analogous to that between snow and ice.

Experimental Method.

The smokes were produced by striking an electric arc in air between electrodes of various common metals. A large inverted funnel was placed immediately over the electrodes. The smokes were drawn from this by suction through a long glass tube of about 2 cm. diameter, lined with a loose sheet of aluminium foil, and which contained a central insulated brass rod. The latter was charged to a high potential by means of an influence machine. The foil was earthed. This constituted the precipitator. The smoke particles collected both on the foil and on the central rod, and when sufficient material had accumulated the precipitated powder was collected from both, placed in a tube, and tightly corked until required for analysis. The metals used were as found in the laboratory: they were not specially selected substances of a high degree of purity.

The material was analysed by the powder method, using a camera of about $3\frac{1}{2}$ in. diameter. In most cases copper $K\alpha$ radiation was employed. The lattice constants were deduced from the measurements of glancing angle θ by means of the general formula

$$\sin^2\theta = Ah^2 + Bk^2 + Cl^2 + Dhk + Ehl + Fkl, \quad . \quad . \quad (1)$$

where h, k, l are the indices to the planes, using the method of successive approximations. The densities were then computed from the formula

$$\rho = 1{\cdot}65 \times 10^{-24}\, n\mathrm{M}/\text{volume of unit cell}, \quad . \quad . \quad (2)$$

where n is the number of molecules in the cell and M their molecular weight, calculated to $O=16$.

It is somewhat difficult to assign limits to the accuracy of the values of ρ deduced from the measurements, although it seems unlikely that many are greater than 1 per cent. in error. The accuracy of the deduced lattice constants not only depends upon the number of variables involved in equation (1), but it also depends upon the number and sharpness of the lines available for measurement. The breadth of the spectrum line is a function of the average size of the particles which produce it. Silver, for example, gave quite sharp lines, whilst the sample of platinum, which produces a similar pattern, gave relatively broad and diffuse lines. The error on this account in the deduced constant is probably less for silver than for platinum where the particles were finer. It should also be remembered that the experimental values given are individual results which have not been examined for accidental and systematic errors. The fact that the observed value $a=4{\cdot}203$ Å. for magnesium oxide happens to be identical with the value given by Wyckoff in the International Critical Tables should not be taken as evidence in support of the tabulated value as against the value $a=4{\cdot}208 \pm {\cdot}001$ recently proposed by Broch(6). The interpretation to be put upon the result is that the crystals in the precipitated smoke have, apparently, an internal structure and a density identical with the crystals used by Broch and the authorities quoted by Wyckoff.

Experimental Results.

The precipitates with one exception proved to be crystalline. Many of the individual results call for little comment.

As was previously known, the readily oxidizable metals give oxides, whilst platinum, silver, and gold give metallic smokes. Magnesium, cobalt, nickel, and cadmium give the simple face-centred cubic monoxides. The deposit from calcium, which was dispersed by Kohlschütter's(1) method from the crater of a carbon arc, contained calcium monoxide and calcium hydroxide. Evidently the smoke dispersed was the monoxide which subsequently absorbed moisture from the air passing through the precipitator during the time involved in collecting the material. Thallium and chromium gave sesquioxides. The former was cubic and the latter the rhombohedral crystal of the α corundum type. Zinc gave the hexagonal monoxide.

The remaining substances may be classified roughly into two groups: smokes which contained more than one substance in the disperse phase and the interesting group which contained oxides possessing polymorphous crystalline modifications. Silver, iron, and copper gave smokes falling in the first group, and aluminium, arsenic, antimony, lead, and carborundum (from which silica is dispersed by Kohlschütter's method) gave oxides of the second group. These smokes are described in greater detail in what follows. The experimental data are collected in Table I.

Silver.—Although silver and platinum both produce metallic smokes, the dispersal process seems more than simple volatilization succeeded by condensation. One smoke from silver was dispersed from electrodes which consisted of pieces of silver about 1 cm. long by 0·5 cm.^{2} in cross-section, mounted on brass rods. During dispersal, the silver ends kept at a red heat. On analysis, the smoke produced gave only lines due to metallic silver. Another smoke was dispersed from electrodes which consisted of silver-foil rolled into the form of a rod. This arc was more difficult to maintain—it ran intermittently and the electrodes obviously kept at a lower average temperature. In addition to metallic silver, the smoke in this case was found to contain a proportion of silver oxide Ag_2O.

Now von Wartenberg(7) has shown, from vapour pressure measurements at high temperatures, that silver is more readily volatilized in oxygen than in hydrogen or nitrogen, and in consequence apparently possesses a higher vapour pressure in oxygen than in the other gases. This he attributes to the intermediate formation of an oxide in the silver vapour, which immediately decomposes again. He actually found traces of oxide in samples of silver distilled

TABLE I.

No.	Metal Used.	Material Dispersed.	Crystal System.	Unit Cell in Å.			Calculated Density.	Comparison Data.				Ref.
				a.	b.	c.		a.	b.	c.	ρ.	
1 ……	Mg	MgO	C	4·203	—	—	3·583	4·203	—	—	3·59	W*
2 ……	Al	$Al_2O_3\ \beta$	H	5·591	—	22·71	3·290	5·63	—	22·63	—	(22)
		?	—	—	—	—	—					
3 ……	SiC †	SiO_2					Amorphous Silica Glass				2·20	(20)
4 ……	Ca †	CaO	C	4·801	—	—	3·343	4·79	—	—	3·37	W
		→ $Ca(OH)_2$	H	3·588	—	4·922	2·226	3·52	—	4·93	2·31	W
5 ……	Cr	Cr_2O_3	H	4·946	—	13·55	5·238	4·94	—	13·57	5·25	
6 ……	Mn †	Mn_3O_4	Tet	8·149	—	9·448	4·709	8·14	—	9·42	—	(23)
7 ……	Fe	$Fe_2O_3\ \alpha$	H	5·031	—	13·74	5·247	5·03	—	13·74	5·25	W
		$Fe_2O_3\ \gamma$	C	8·366	—	—	5·400	8·37	{Fe_3O_4}	—	—	W
8 ……	Co	CoO	C	4·247	—	—	6·455	4·24	—	—	6·49	W
9 ……	Ni	NiO	C	4·171	—	—	6·79	4·172	—	—	6·75	W
10 ……	Cu	CuO	Tri	3·74 α 85° 21′	4·67 β 86° 25′	4·67 γ 93° 35′	6·503 —	3·74 α 85° 21′	4·67 β 86° 25′	4·67 γ 93° 35′	6·48	W
		Cu_2O	C	4·254	—	—	6·132	4·28	—	—	6·02	W
		?	—	—	—	—	—					
11 ……	Zn	ZnO	H	3·250	—	5·217	5·623	3·25	—	5·23	5·61	W
12 ……	As	As_2O_3	C	11·05	—	—	3·869	11·06	—	—	3·86	W
13 ……	Ag	Ag	C	4·077	—	—	10·50	4·079	—	—	10·49	W
		Ag_2O	C	4·747	—	—	7·14	4·72	—	—	7·27	W
14 ……	Cd	CdO	C	4·687	—	—	8·226	4·72	—	—	8·06	W
15 ……	Sn	SnO_2	Tet	4·747	—	3·188	6·915	4·72	—	3·16	7·07	W
		?	—	—	—	—	—					
16 ……	Sb	Sb_2O_3	R	12·00	3·347	8 489	5·578	—	—	—	5·566	(18)
17 ……	W	WO_3	R	7·336	10·48	4·18	7·146	—	—	—	7·2	(25)
18 ……	Pt	Pt	C	3·914	—	—	21·47	3·913	—	—	21·5	W
19 ……	Au	Au	C	4·065	—	—	19·37	4·064	—	—	19·4	W
20 ……	Tl	Tl_2O_3	C	10·53	—	—	10·31	10·57	—	—	10·2	W
21 ……	Pb	PbO	R	5·467	4·742	5·862	9·688	5·50 ±·02	4·72 ±·03	5·880 ±·003	9·64	(26)
22 ……	Bi	Bi_2O_3	Tet	5·462	—	5·619	9·128	—	—	—	8·8–9·0	(25)

* The reference W is to Wyckoff, "X-ray Diffraction Data," 'International Critical Tables,' vol. i. 1926.

† Dispersed from the crater of a carbon arc.

in oxygen, which supports the hypothesis. The formation of a silver smoke in air, therefore, seems to involve the equilibrium of a system which perhaps may be represented by the reaction

$$2Ag_2 + O_2 \rightleftharpoons 2Ag_2O. \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Since the oxide is decomposable by heating, we should expect the reaction to move towards the left at high temperatures. At the temperature of the silver-foil arc, the equilibrium amount of oxide will be greater than at the red heat of the metallic arc. Thus the difference in the compositions of the two smokes seems explicable if we suppose that the disperse system is formed at a temperature approaching that of the arc and that the equilibrium proportions of the solid phases are at least partially conserved by the quenching action of the air currents which flow past the electrodes when the arc is running.

Copper.—An analogous effect is found with copper. The copper arc gave a mixture of cupric oxide and cuprous oxide. The former seemed in excess. In addition, there were a few faint lines on the film which were not identified. The equilibrium of the system cupric oxide, cuprous oxide, oxygen, has been studied in detail by Smyth and Roberts (8). It has a eutectic point at 1080°·2 C. and at 402·3 mm. pressure, where four phases are in equilibrium, both solid oxides, oxygen gas, and a liquid eutectic of both oxides. At lower temperatures both oxides remain solid and the reaction

$$4CuO\,(\text{solid}) \rightleftharpoons 2Cu_2(\text{solid}) + O_2\,(\text{gas}) \quad . \quad . \qquad (4)$$

takes place. At higher temperatures and at pressures less than 402·3 mm. fusion occurs and the reaction is

$$4CuO\,(\text{liquid solution in } Cu_2O) \rightleftharpoons 2Cu_2O(\text{solid}) + O_2(\text{gas}). \quad . \quad . \quad . \qquad (5)$$

The dissociation pressure of reaction (4) at 1026° C. and of reaction (5) at 1135° C. is equal to 153 mm., the partial pressure of oxygen in air. If, therefore, the smoke particles are formed by a condensation process (the usual assumption), and we may further assume that when formation occurs the medium has the same oxygen content as normal air, some of the particles must have formed at a temperature higher than 1026° C., the temperature at which cupric oxide begins to dissociate when heated in air. The presence of cuprous oxide in the smoke shows that the subsequent cooling of the disperse system, as its temperature fell below 1026° C. where reaction (4) proceeds from right to left, must have been rapid. The particles were quenched before the reaction could pass to completion.

Thus the nature of the material dispersed from a copper arc depends upon the temperature at which the particles are formed and the partial pressure of the oxygen present in the medium on formation *. When the latter is 153 mm. it is clear that below 1026° C. we should obtain a smoke of cupric oxide particles only. Temperatures between 1026° C. and 1135° C. are required to produce cuprous oxide and with temperatures greater than 1135° C. we may get solidified particles from the phase represented by the left-hand member of equation (5). These particles may be responsible for the weak unidentified lines in the spectrum of the precipitated smoke. It seems clear that the actual formation of the particles as a disperse system occurs at a high temperature and close to the electrodes of the arc. But the temperature of the arc is known to vary at different parts, so even if, as it seems probable from their small mass, the particles on formation are in thermodynamical equilibrium with the adjacent medium, it is impossible to say whether the mixture in the smoke arises from contributions suddenly cooled from different parts of the arc which are at different temperatures, or whether it is due to the reactions (4) and (5) becoming arrested by the cooling before reversion to cupric oxide is completed. In either case, the majority of the smoke particles in the sample examined must have been formed at temperatures in the neighbourhood of 1000° C.

Gold.—Gold, the remaining metal of the copper group, was dispersed from thick foil rolled into the form of rods and used as electrodes in the arc. The lines in the spectrum from the deposited smoke were all due to metallic gold.

Iron.—The smoke from iron electrodes consisted of a mixture of iron oxides. All the lines in the spectrum could be accounted for on the supposition that the deposit consisted of a mixture of paramagnetic ferric oxide and ferro-ferric oxide. The latter (magnetite) is cubic and the former is rhombohedral, isomorphous with $\alpha\ Al_2O_3$. Like Al_2O_3, ferric oxide is polymorphous. Magnetite on oxidation to ferric oxide at comparatively low temperatures is converted into the ferromagnetic iron oxide $\gamma\ Fe_2O_3$, which is reported to give an X-ray spectrum identical with that from magnetite itself, the spacings agreeing with one-tenth of one per cent.(9). Ferromagnetite ferric oxide γ Fe_2O_3 is permanently transformed into the commoner paramagnetic α Fe_2O_3 at a higher temperature, the exact value of which depends largely on its mode of preparation(10). Thus if the oxidation of iron to ferric oxide in the dispersal process occurs with Fe_3O_4 as an intermediate product, it is possible that the smoke contains a proportion of γ Fe_2O_3, but this apparently cannot be decided from X-ray data alone.

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* If the partial pressure were half the normal, *i. e.*, 77 mm., the temperatures change from 1026° C. and 1135° C. to 989° C. and 1161° C. respectively.

A test with potassium ferricyanide failed to confirm the presence of ferrous iron in the precipitated smoke. Hence the smoke must consist of a mixture of α Fe_2O_3 and γ Fe_2O_3.

Since magnetite and the ferromagetic iron oxide have substantially the same susceptibility—some 10,000 times that of α Fe_2O_3—the magnetic properties of the smoke and of the deposit from it will be practically the same as if the smoke consisted of a mixture of magnetite Fe_3O_4 and the non-magnetic ferric oxide.

The occurrence of γ Fe_2O_3 is therefore of interest in connexion with a magneto-optical effect with fumes from an iron arc, described a few years ago by Elihu Thomson(11). The smoke particles from an iron arc tend to form thread-like complexes on aggregation. Normally, owing to Brownian movements, the complexes in the smoke will be oriented at random, but in the presence of a magnetic field the magnetic aggregates will tend to lie along the lines of force, thereby producing a vectoral or anisotropic property in the smoke. It is to be expected that such a property will be revealed by the optical behaviour of the system.

Thomson illuminated the smoke by a beam of sunlight and arranged to produce a magnetic field in it with the lines of force perpendicular to the incident beam. When viewed in a direction making a small angle with the beam, the smoke becomes luminous when the field is on and invisible when the field is off. The light diffracted from the luminous cloud in a plane perpendicular to the lines of force is partially polarized. On the assumption that the particles were magnetic, Thomson attributed the effect to the lining up of the chains of particles under the influence of the field. The increased diffraction from the oriented particles accounts for the extra visibility when the field is on. On removal of the magnetic field, Brownian movement obviously destroys the structure and the visibility of the smoke diminishes. The results of the X-ray analysis remove the need for the assumption. They further explain another effect observed by Thomson. This, perhaps, is best described by a quotation from the letter to 'Nature':—

"Moreover, the very curious fact was discovered by me, that the fumes from the iron arc were composite so far as analysis by the polarizing prism was concerned. The bluish-coloured smoke arising gave but little effect, but there was with it a yellowish-grey fume, which was highly luminous in one position of viewing by the prism, and invisible when the prism was at right angles to that position. This indicates complete polarization when the field is on for the light diffused from the particles in the yellowish-grey fumes. This is an extraordinary effect for which no explanation suggests itself."

We have seen that the fumes are composite so far as analysis by X-rays is concerned. They contain the magnetic $\gamma\,Fe_2O_3$ and the non-magnetic $\alpha\,Fe_2O_3$. Evidently the blue-coloured fume, which presumably is given off from the core of the arc, consists mainly of paramagnetic ferric oxide particles, whilst the yellowish-grey fume consists of the ferromagnetic oxide. The difference in colour, of course, depends upon the size of the particles, the $\alpha\,Fe_2O_3$ particles being the smaller. The difference in size of the particles of the two substances should be manifest on the powder photograph, for the smaller $\alpha\,Fe_2O_3$ particles would give lines which were more broad and diffuse than those due to the magnetic oxide. This actually appears to be the case, but without accurate measurement the point cannot be fully decided. The higher temperature of the central portion of the arc is conducive to greater chemical activity and to a greater concentration of dispersed matter. By von Wiemarn's law of corresponding states, it is to be expected that the resulting degree of dispersion of the paramagnetic particles will be greater and therefore the average size of the particles less than in the fume from the outer and cooler portions of the arc. The separation of the fume as revealed by its colour and the magneto-optical effects suggests that the γ oxide formed results from oxidation of the iron in the cooler portions of the arc. We should obtain a lower limit to the temperatures at which the smoke particles are formed if we assumed that the $\gamma\,Fe_2O_3$ results from the intermediate formation of Fe_3O_4. Welo and Baudisch (9) obtained $\gamma\,Fe_2O_3$ by heating Fe_3O_4 to 220° C. in air. Sosman and Hostetter (12) found that magnetite begins to oxidize at an observable rate at 300° C., but it appears (10) that different varieties of magnetite exhibit great differences in their resistance to oxidation, and therefore in the temperatures necessary to ensure completion of the reaction. It seems as difficult at present to fix a temperature of formation of $\gamma\,Fe_2O_3$ as it is give a temperature for its transformation into $\alpha\,Fe_2O_3$.

According to O. Wiener (13), if a substance consist of aggregates of parallel rods, it will show double refraction. Virtually such aggregates behave as uniaxial crystals. This seems the type of structure produced in an iron smoke by a magnetic field. Hence we may expect an iron smoke to show double refraction. Tieri (14) finds that it gives a positive birefringence. He also noted that a copper smoke in a sufficiently intense field was doubly refractive. This is undoubtedly due to the paramagnetism of cupric oxide (15).

Platinum.—The electrodes of the platinum arc consisted of platinum-foil rolled into the form of rods. Like the silver arc between foil electrodes, the platinum arc was difficult to maintain and probably ran at a temperature lower than would have obtained had the electrodes been solid rods of the metal. Only lines due to metallic platinum were found on the film. They were diffuse, as if the particles were very fine. The result accords with the orthodox view that platinum produces a metallic smoke. According to Roberts (24), however, a clean platinum wire when heated produced nuclei (particles) only in the presence of oxygen, and not in its absence. He attributed this to the intermediate formation of an oxide and adduces other experimental evidence in support of the hypothesis. Platinum would then behave like silver, which seems plausible. The subject might repay further investigation.

Lead.—Lead gave only lines due to the rhombic yellow monoxide. This modification is formed when the fused oxide is cooled. It is unstable and turns into the red modification at room temperatures, the transformation being accelerated apparently by rubbing (16). It is probably the modification which is formed from lead carbonate by heating at 600° C. The X-ray spectrum, which was taken immediately after the smoke had been precipitated, showed no traces of the tetragonal red monoxide.

Arsenic and Antimony.—The smokes from these metals consisted of the sesquioxides. These are said to be isodimorphous. Both exist in a cubic form. Sb_2O_3 possesses an orthorhombic modification (valentinite) and As_2O_3 has an orthorhombic (Dana (17)) or a monoclinic (pseudorhombic) form (18). Both forms of As_2O_3 are obtained by sublimation. According to Dana, the prismatic form is only obtained at a temperature above 200° C. and the cubic form at one much lower. Valentinite is the high temperature form of Sb_2O_3. The structures of the cubic forms have been given by Bozorth[19], but no data about the other modifications seem available. The cubic form was obtained with the smoke from arsenic, but not with the smoke from antimony. The latter appeared to be orthorhombic. The number of lines obtained in the spectrum, however, was insufficient to give reliable constants by the method of successive approximations, so the observations were reduced by assuming Dana's values for the axial ratios $a : b : c = 3{\cdot}587 : 1 : 2{\cdot}536$. Apparently the disperse phase in the case of arsenic was formed at a temperature not greater than 200° C. This seems plausible. Comparatively large pieces of arsenic were used as electrodes in the arc and the smoke was found to be very readily produced. Contrary to what occurred with antimony, the arsenic electrodes hardly got warm.

The supposition that dispersal occurred at a relatively low temperature in the case of arsenic receives some support from the colour of the precipitated smoke, which was grey and not the usual white associated with arsenious oxide. The colour probably arises from traces of metallic arsenic, although the quantity present was insufficient to produce a recognizable spectrum.

Aluminium.—The smoke from aluminium consists of alumina. Al_2O_3 crystallizes in three forms known as α, β, and γ corundum. The first is rhombohedral (ruby type), isomorphous with the crystals of Fe_2O_3 and Cr_2O_3 found in the smokes from iron and chromium ; the second is hexagonal, and the third is said to possess the same structure as ferromagnetic Fe_2O_3, so is presumably cubic. The spectrum of the precipitated smoke from aluminium electrodes showed no lines which could be attributed to the commoner rhombohedral form. With the exception of six weak lines, the spectrum agreed with that to be expected from β corundum. The six weak lines were not identified with certainty. They are not due to metallic aluminium, and, since even the commercial metal is now 98–99 per cent. pure, it seems unlikely that they are due to impurities in the aluminium. Their positions agreed tolerably well with possible reflexions from a cubic lattice with $a = 6{\cdot}53$ Å. The smoke therefore consists mainly of β corundum, a hexagonal crystal, with possibly a small admixture of the γ type.

Silica.—This substance was prepared by the combustion of carborundum SiC in the crater of a carbon arc. The smoke gave a translucent white deposit which on analysis failed to give a characteristic spectrum with either CuKα or Fe radiation. A close examination of the film which had received the longest exposure revealed a few faint lines which normally would almost certainly have passed unobserved. These, however, were all found to agree with reflexions from carborundum I. No trace whatever was found of the spectra from either α or β quartz, α or β tridymite, or β cristobalite. The material is, therefore, amorphous silica containing traces of carborundum as impurity. According to the phase diagram of Fenner (20), the amorphous form of silica—silica glass—is the modification which is stable at temperatures greater than 1625° C. It seems reasonable to infer that the silica smoke was produced at a very high temperature. It is difficult to disperse and requires a high current density, but once dispersal has commenced smoke production is not so difficult to maintain. The retention of the phase as the smoke cools is materially assisted by the sluggishness exhibited by silica in its changes from one state to another.

Bismuth.—The bismuth arc gave a smoke of Bi_2O_3. This is said to be polymorphous; crystals attributed to the cubic system and to the orthorhombic have been described (Groth), but no X-ray data about the substance seems available. The spectrum obtained from the smoke with CuKα radiation consisted of about 53 lines which could all be accounted for as reflexions from a tetragonal lattice. As it is difficult to be certain from a powder photograph alone that the lines are not due to a mixture of two types of crystal, the lattice constants given in the table are offered as a possible unit cell.

Tungsten.—Tungsten was dispersed by fusing a wire of the metal in air with a heavy current. About 120 lines were measured on the film, which was taken with CuKα radiation. The absence of data upon a single crystal of the trioxide makes it impossible to check the identification of the planes responsible for the lines. Hence the constants of the orthorhombic lattice given are those of a possible unit cell. The ratios of the constants, $a:b:c=0{\cdot}7000:1:0{\cdot}3988$ happen to agree with the axial ratios given by Nordenskiöld for tungstite and quoted by Dana (15), viz. $0{\cdot}7002:1:0{\cdot}3991$.

Manganese.—According to Kohlschütter and Tüscher, the precipitated smoke from manganese consists of a mixture of manganese sesquioxide Mn_2O_3 and manganese dioxide MnO_2.

The sample examined by X-rays, although prepared by the same method, was found to consist of the red manganese oxide Mn_3O_4. As Mn_3O_4 is the most stable of the oxides and is formed when either Mn_2O_3 or MnO_2 is strongly heated, the discrepancy may be merely a temperature effect. All the lines observed were accounted for and no trace was found of lines attributable to MnO_2 or Mn_2O_3.

Tin.—The analysis of the precipitated smoke from tin electrodes was the least satisfactory of all attempted. The smoke, which is probably wholly stannic oxide, is produced at a relatively low temperature, probably not much higher than the melting-point of tin 232° C.; for as soon as the electrode ends soften they drop off under their own weight and extinguish the arc. This is conducive to the formation of unstable modifications of SnO_2 if such exist. The commonest form of SnO_2 is cassiterite, a tetragonal crystal similar to rutile (TiO_2), but two other modifications have been reported—a rhombic, analogous to brookite (TiO_2), and a pseudohexagonal similar to tridymite (SiO_2). The powder photograph showed that the precipitate did not consist of cassiterite, although spacings were present which agreed closely with all those given by cassiterite. The material may therefore consist of the common tetragonal form of SnO_2 with possibly another modification present as well. This is the result tabulated but pending further investigation it is given with great diffidence. It shows, however, that the interatomic distances in the crystalline smoke particles are closely similar to those in cassiterite, so the respective densities cannot differ greatly.

The Densities of the Particles.

It will be seen from the results in Table I. that the measured constants closely agree with the comparison data. The variation is no greater than that observed amongst the values published by different observers for the same crystal. The size of the unit cell in constituent particles of any smoke is therefore identical with that in a macroscopic crystal of the same material. Moreover, the relative distribution of intensity amongst the spectral lines for any given substance was found to be the same for both the smoke particles and for the crystallized material wherever published data were available for reference. Hence the atoms occupy similar positions within the unit cells in both cases. It follows that the homogeneous particles in the precipitated smokes have the normal density of the same material when it occurs as a crystal.

The results also show that the crystalline smoke particles are usually formed at a high temperature, probably close to the pole pieces of the arc, and that they cool rapidly as they leave it. The particular crystalline structure acquired on formation is thereby conserved, with the result that the dispersoid from polymorphous substances usually possesses the modification which is stable at high temperatures.

The results as a whole suggest that the formation of the primary particles of a smoke takes place suddenly during the condensation process and under equilibrium conditions both internally and externally with respect to the particle. The external conditions determine the chemical nature of the particle and are controlled by the thermodynamical equations appropriate to the chemical reactions occurring ; the internal equilibrium determines the molecular structure of the particle and is, presumably, governed by the laws of lattice dynamics.

Although X-rays reveal the internal structure, they give no information about the shape of the particles. In almost all cases the particles are of ultramicroscopic size and therefore give diffraction disks and not images when examined optically. In the past the ultramicroscopic particles have been considered spherical—mainly, perhaps, as a matter of convenience. We expect liquid particles like oil drops to be spherical owing to the action of surface tension, but as many of our oxides from their known chemical properties, *e. g.*, Ag_2O, CuO, can never have been liquid, we cannot suggest in these cases that the particles are solid spheres resulting from sudden chilling after fusion.

From a crystallographic standpoint there is no reason why the ultramicroscopic particles should not be facetted and possess external forms precisely like macroscopic crystals grown under similar conditions. The photomicrograph, fig. 1 of the paper of Paterson and Whytlaw-Gray (5) shows that the larger particles in the deposit from a magnesium oxide smoke are facetted. Kohlschütter and Tüscher found that the particles in the smoke from arsenic were microscopic crystals. By regulating the rate of smoke production they obtained minute crystals from sparse antimony oxide smokes, whilst from denser smokes the particles appeared smaller and showed no recognizable form. A change in size only, in the direction demanded by von Weimarn's law of corresponding states, seems adequate to explain the appearance of the precipitate in the latter case.

The manner of aggregation of the particles provides evidence bearing on this point. It is well established that after formation the primary particles in a smoke disappear by a process of aggregation. If this takes place along a concentration gradient or in an electric field the resulting aggregates are thread-like. This peculiarity has long been known, and was observed in greater or less degree with all the substances examined. From their behaviour in a current of air, when one end is fixed on, say, an electrode of the electric field, it is clear that the filaments can withstand tension, although they are probably never as strong as a spider thread. In the case of cadmium oxide, where they are obtained with comparative ease, it has been shown that the individual particles in the chains are oriented in the direction of a crystallographic axis(21). It seems probable that this occurs in all cases. Taking into consideration that in the chain-like filaments we are dealing with the arrangements of the individual particles, irrespective of size, and that the strength of the filament must be determined by the strength of its weakest link, this behaviour seems inexplicable if we assume that the particles are spherical, each touching its neighbour at a mathematical point. If, however, the particles have the external forms of crystals, we get surfaces in contact; in the case of cadmium oxide, like faces (mostly dodecahedron faces) are in contact, and the growth of these structures seems inevitable.

Until, therefore, we obtain unimpeachable evidence to the contrary, we may assert that the primary particles are bounded by plane faces. The particles in the smokes examined, with the sole exception of silica, are therefore crystals of the dispersoid, similar in internal structure and external appearance with the specimens exhibited by crystallographers. They differ mainly in the matter of size.

In conclusion, I wish to thank Mr. C. H. Gregory for his valuable assistance in obtaining powder photographs, and Prof. W. L. Bragg for the interest he has taken in the work.

SUMMARY.

The precipitated smokes dispersed by an arc from about twenty common metals have been examined by the powder method of X-ray analysis and found to be crystalline. The particles in a smoke of SiO_2 dispersed from carborundum were amorphous and consisted of silica glass. Platinum and gold gave metallic smokes.

Smokes which consist of oxides which are polymorphous, usually give the modification which is stable at high temperatures. The smokes from copper and iron give mixed oxides. This seems due to dissociation in the first case and to low temperature oxidation in the second. These results indicate that the formation of the smoke particles is completed at a high temperature and in the immediate neighbourhood of the hot electrodes.

The results for iron are shown to complete the explanation offered by Elihu Thomson of a magneto-optical effect observed with the fume from an iron arc.

The densities of the crystalline particles in the smokes are normal. The abnormally low values found by previous investigators, using other methods, are attributed to the mode of aggregation of the particles.

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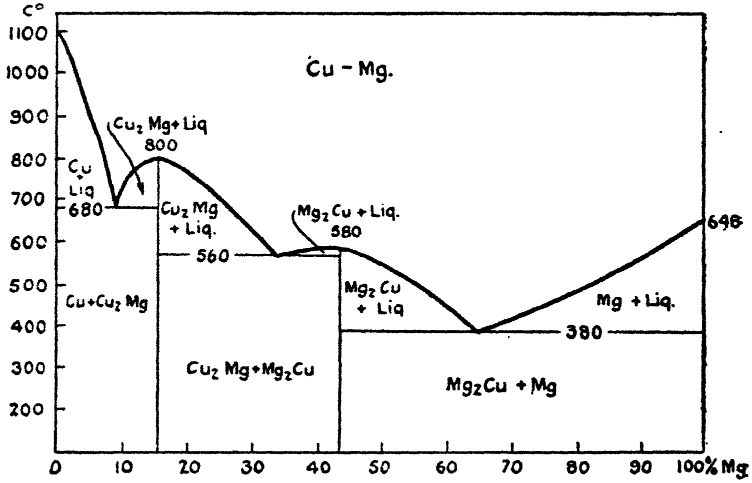
CXXVI. *An X-Ray Investigation of the Copper-Magnesium Alloys.* By GEOFFREY GRIME, *M.Sc.*, *and* W. MORRIS-JONES, *M.A.*, *M.Sc.* (*Department of Physics, University College, Swansea*) *.

INTRODUCTION.

THE most thorough investigation of the copper-magnesium system of alloys is that of Sahmen †. His work, published in 1908, led him to the equilibrium diagram given in fig. 1. This diagram is taken as the basis of comparison in the present investigation.

Fig. 1.



Sahmen's equilibrium diagram.

The diagram is a simple one, and consists of three sections, each of which may be considered as a separate system. The systems are $Cu-Cu_2Mg$, Cu_2Mg-Mg_2Cu, and Mg_2Cu-Mg. Each of the sections shows the behaviour of two constituents soluble in each other in all proportions when hot, but insoluble when cold. The system has, therefore, two maxima at compositions represented by the formulæ Cu_2Mg and Mg_2Cu, and three minima at intermediate eutectic compositions. The metallurgical data all point to the existence of intermetallic compounds at the compositions represented by the maxima.

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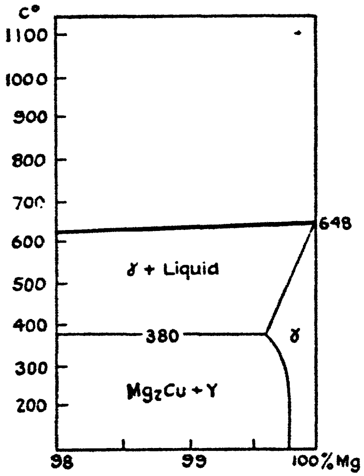
* Communicated by W. Morris-Jones, Senior Lecturer in Physics, University College, Swansea.

† *Zeit. Anorg. Chem.* lvii. pp. 1-33 (1908).

An earlier work by Boudouard * supplies the only evidence against the form of the curve. He found an additional maximum corresponding with a composition CuMg, but was unable to isolate the assumed compound. Neither diagram (Sahmen's nor Boudouard's) shows any regions of solid solutions—both are ideal examples of their type.

Hansen †, by a microphotographic investigation, carried out in 1924, on the magnesium-rich alloys, claimed to have proved that magnesium can hold copper in solution at ordinary temperatures to the extent of something approaching 0·2 per cent. This, if confirmed, would result in the modification of the magnesium end of the diagram to the form given in fig. 2. Jenkin, however, in the discussion ‡ on the above-mentioned paper, disputed the accuracy of these inferences, and put the solubility of copper as very much less. From examination of the microstructure of alloys prepared and examined by him, he inferred that the solubility of copper in magnesium is less than 0·04 per cent.

Fig. 2.



Mg end of diagram according to Hansen.

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* *Compt. Rend.* cxxxv. pp. 794–796 (1902); cxxxvi. pp. 1327–1329 (1903).

† Journal of Institute of Metals, p. 93 (1927).

‡ *Loc. cit.*

The present investigation was undertaken as it was thought that an X-ray study of the system, while of interest as a problem in crystal analysis, would yield evidence of the formation of solid solutions undetected by metallurgical investigation; and would, in particular, throw light on the unsettled problem of the solubility of copper in magnesium. The lattice of such solid solutions would differ slightly in dimensions, but not in crystallographic system, from those of the pure solvent. A series of eight alloys, of composition ranging from pure copper to magnesium, were therefore prepared and their crystal structures examined by the X-ray powder method.

Preparation of Alloys.

The alloys, containing from 0 per cent. to 47 per cent. magnesium, were prepared by the method adopted by Boudouard *.

The materials used were electrolytic copper and magnesium of high purity. The copper was melted under a layer of charcoal in a salamander pot, in which scrap magnesium had previously been melted to take up any active material from the walls, and to form a protective lining. When molten, the metal was stirred with a carbon rod, to get rid of oxygen, and then most of the charcoal layer was scraped off. Sodium chloride, to form a molten layer about half an inch thick, was placed in the pot. When the metal and flux were completely fluid once more, the magnesium was introduced in large pieces and held beneath the surface of the copper with a tongs until liquid. After the first piece had been introduced, the temperature of the furnace was allowed to decrease, for, as may be seen from the equilibrium diagram, the melting-point of the alloy drops very steeply with increasing magnesium content. Lowering the temperature prevents loss of magnesium by oxidation, which is very likely to take place if the furnace is too hot. When the calculated weight of magnesium, with a few grams over to allow for oxidation, had been introduced, the alloy was stirred, left in the furnace for a few minutes, and then withdrawn and allowed to cool in the pot. A wind furnace was used, and ingots of 200–300 grms. were prepared each time.

In preparing alloys having a higher magnesium content the method of Cook and Jones † was employed.

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* *Loc. cit.*

† Journal of Institute of Metals, pp. 36, 157 (1926).

The alloys were made in an iron crucible, in a small gas furnace capable of raising the temperature of a small melt to about 800° C. The copper was introduced in the form of a 64-per-cent. copper-magnesium alloy, which was melted up with the calculated amount of magnesium under a flux of one part of magnesium chloride to one part of potassium chloride.

This flux melts between 400–500° C., which is lower than the melting-point of any of the alloys. It therefore covers the whole charge with a protective layer of flux while melting takes place. Sodium chloride cannot be used in this method as its melting-point is considerably above that of the alloys to be prepared.

The iron pot was first heated up and scrap magnesium melted in it, as before, to form a coating. The flux, which is very deliquescent, was prepared fresh each time by heating up the constituents together on an iron ladle until all the water had been driven off and the flux had fused. It was then poured on to a cold iron slab and, when cold, was powdered up ready for use. The charge, consisting of the calculated weights of magnesium and the alloy, broken into small pieces, was introduced into the crucible and covered with a layer of flux—about 3–4 per cent. by weight of the charge—this being the proportion found most suitable by Cook and Jones *. The crucible was covered by a lid and raised to a temperature sufficient to melt the magnesium, and kept there until, on stirring, the liquid felt perfectly uniform. The crucible was then withdrawn from the furnace and allowed to cool.

For those alloys whose density was required, the process of double melting was resorted to, in order that the ingots might be sound. The alloy was allowed to solidify, and was then re-melted quickly and allowed to cool to room temperature. This process gets rid of the peculiar radially-disposed blow-holes, which are present in the once-cooled copper-magesium alloys.

The composition of the alloys was determined by the estimation of the copper-content, the magnesium being estimated by difference, as this involves less error than determining it directly.

The copper was estimated by an electrolytic method, using a rotating cathode. The platinum cage, forming the cathode, was rotated by a small electric motor. A second stationary electrode of platinum disposed co-axially about the cathode

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* *Loc. cit.*

formed the positive pole. The solution, containing 1 gram of the alloy dissolved up in nitric acid, generally took about an hour and a half to be electrolysed. From the weights of alloy taken, and the copper deposited on the cathode, a simple calculation gave the percentage composition of the sample. The densities of the alloys were determined by the suspension method, using small polished specimens with acetone as the immersion fluid. The composition and densities of the alloys are given in Table I.

Method of X-Ray Analysis.

The well-known powder method of Hull was used in the investigation. In this method a disordered mass of very fine crystals is placed along the axis of a cylindrical camera, and when irradiated with a narrow beam of X-rays gives rise to a series of lines on a strip of photographic film disposed around the circumference of the cylinder.

The information furnished by the photograph consists of interplanar distances in the crystal structures, together with the intensities of the lines produced by the set of planes having these interplanar distances.

Details of the apparatus used in the present investigation have been given in a previous paper *, and need not be described here.

The procedure employed in preparing the powder was the following.

The material was broken up into small pieces and ground down as fine as possible in a small agate mortar. It was found that the alloys of high magnesium-content attacked the mortar during grinding, leaving a thin skin of copper colour on the surface—probably due to the combination of the active magnesium with the material of the mortar, when heated by grinding. This was remedied by grinding under acetone, which kept the powder cool. The finest particles were then separated by a process of decantation. The powder was shaken round with acetone in a beaker, and the top portion, containing the lightest particles, decanted off on to a filter-paper and there collected.

Alloys which, owing to their ductile nature, could not be broken up by grinding were rubbed off with fine emery-cloth, and the process of decantation carried out on the powder so obtained.

A cylindrical glass fibre was situated along the axis of the camera. The powder was painted on this fibre with an organic adhesive to the thickness of 1/10 mm., resulting in a powder-coated rod of diameter 0·70 mm. Its diameter was measured each time with a travelling microscope to ensure that the variation should not exceed 0·05 mm. An exposure of two to three hours was generally sufficient for a good photograph. The developed photograph was mounted on the table of a travelling microscope, and the distances of the lines from the central zero position were measured. A correction has to be applied for the diameter of the cylindrical glass fibre. This is best done by standardising the camera with the lines from a lattice of accurately known dimensions. Such a standardisation will rectify all permanent errors of the camera, such as faulty centring of the specimen and imperfect shape of the camera.

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* Morris-Jones & Evans, Phil. Mag. iv. (December 1927).

Sodium chloride, which gives an excellent pattern of evenly-spaced intense lines, was used for the standardisation. Its lattice, which is accurately known, is cubic with a base $a_0=5{\cdot}628$ Å.U.

From the corrected distances on the film the diffracting angles θ_1, θ_2 etc. were calculated, and from these angles the interplanar spacings d/n were found, using the formula

$$\frac{\lambda}{2}=\frac{d}{n}\sin\theta.$$

These spacings, together with the intensity of the lines, constitute the information available from powder photographs, and the crystal structure has, if possible, to be deduced from it.

For the accurate determination of the dimensions of the crystal lattice, only those lines between 40 and 60 mm. from the zero position were used. This range was chosen as furnishing the most accurate measurements, from the following considerations:—

(*a*) It was found from experience that up to 80 mm. from the centre of the films the maximum error in marking the films amounted to 0·1 mm. It is therefore of advantage to use those lines in this range which are furthest from zero, since the proportional error in measurement is then least.

(*b*) The lines diffracted at large angles come off the broad surface of the specimens nearest the slit, and are diffuse and difficult to mark accurately.

The region 40 to 60 mm. from zero offers the best compromise between large deviation and fineness of line, and has been used for the accurate determination of the unit cell whenever more than two lines were present in that region.

Another factor in the accuracy of measurement is the variation of absorbing power in the different substances investigated. Assuming that the diameter of the specimen is the same in each case, as was actually ensured by measurement, then the lower the absorbing power of the alloy, the further in towards zero are the lines, and the correction curve would only hold good if both powdered specimens (after being painted on) possessed the same absorbing power. In practice, the effect was reduced to a minimum by powdering the substance very finely to ensure a high surface-density. Under these circumstances, and with the soft copper radiation used, the diffraction could be considered as taking place from practically the surface of the cylinder. Observing these precautions, and using lines between 40 and 60 mm. from the zero position, the accuracy may be estimated as within 1/6 of 1 per cent.

RESULTS.

The chemical composition of the eight alloys, as determined by analysis, are given in Table I. Two photographs were taken of each alloy; the measurements given in the appropriate tables are the mean of the results from the two films. The second exposure was taken to prevent the possibility of error due to the positioning of the film.

The results of the X-ray investigation of the crystal structures confirm, in the main, the equilibrium diagram of Sahmen, *i. e.*, that it consists of three sections and shows maxima at the compositions corresponding with the formulæ Cu_2Mg and Mg_2Cu. No evidence of Boudouard's third compound CuMg was obtained. In addition, the X-ray investigation revealed two new regions of solid solution. These were :—

(*a*) A solution of magnesium in copper up to approximately 3 per cent. magnesium.

(*b*) A region of solid solution extending on both sides of the Cu_2Mg composition.

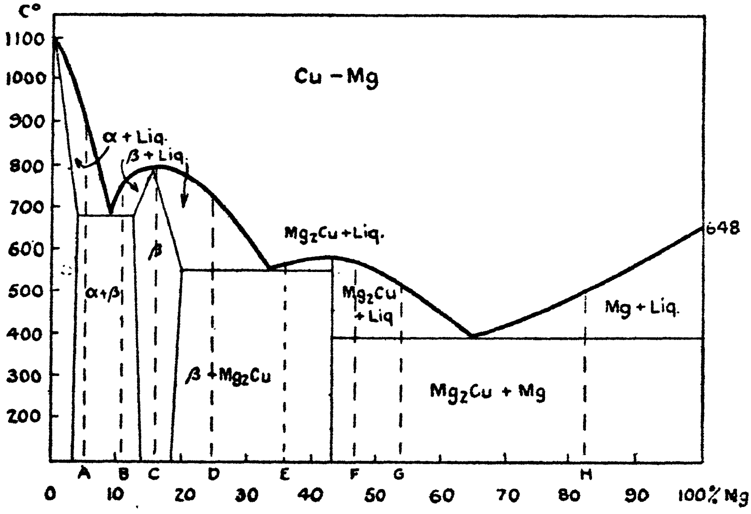
In every other particular the original diagram was corroborated. No trace of solid solution could be detected at the magnesium end. Variation in the position of the lines, due to the magnesium lattice, was particularly small.

An examination of column 5 of Table I. shows that the dimensions of the magnesium lattices determined from alloys G and H differ from those of the pure metal by only one part

TABLE I.

Alloy.	Composition.	Density.	Type of lattice.	Length of base (in Å.U.).
	per cent. Mg.			
Copper	0	8·94	Face-centred cubic.	$a_0 = 3{\cdot}610$
A	5	8·61	Face-centred cubic.	$a_0 = 3{\cdot}634$
B	11	6·64	Mixture of two face-centred cubic systems.	$a_0' = 3{\cdot}630$ $a_0'' = 7{\cdot}003$
C	16	5·72	Face-centred cubic.	$a_0 = 7{\cdot}034$
D	25	5·02	Face-centred cubic and hexagonal.	$a_0' = 7{\cdot}059$ $a_0'' = 5{\cdot}288$
E	36	3·90	Face-centred cubic and hexagonal.	$a_0' = 7{\cdot}066$ $a_0'' = 5{\cdot}276$
F	47	3·18	Hexagonal.	$a_0 = 5{\cdot}281$
G	54	3·05	Mixture of two hexagonal systems.	$a_0' = 5{\cdot}280$ $a_0'' = 3{\cdot}205$
H	82	2·22	Mixture of two hexagonal systems.	$a_0' = 5{\cdot}280$ $a_0'' = 3{\cdot}205$
Magnesium	100	1·74	Hexagonal close packed.	$a_0 = 3{\cdot}206$

Fig. 3.



Equilibrium diagram as modified by X-ray investigation of the system. Dotted verticals are erected at compositions investigated.

in 3200. The solubility of copper in magnesium is therefore exceedingly small—probably the order suggested by Jenkin.

The equilibrium diagram modified by the results of the X-ray investigation is given in fig. 3. The dotted verticals on the diagram show the compositions at which photographs were taken.

The α Phase.

The α phase (see fig. 3) was investigated with the aid of powder photographs of copper, and of alloys A and B. The data are given in Tables I., II., III., and IV.

TABLE II.—Copper.
(Face-centred cubic.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_β	111	W.	2·082	2·084
K_α	111	St.	2·084	2·084
K_α	100	St.	1·804	1·805
K_α	110	St.	1·275	1·276
K_α	131	St.	1·089	1·088
K_α	111 (2)	M.	1·042	1·042

NOTE.—In Tables II.-XI. the first column states the quality of the copper radiation; the second, the indices of the plane spacings referred to rectangular or hexagonal axes according to the type of structure found; the third, the intensities of the lines on the photograph; and the fourth gives the plane spacings obtained from measurements on the films. The fifth column gives the calculated plane spacings for the respective lattices obtained.

The intensities of the lines are denoted by the symbols St.=strong; M.=medium; W.=weak; V.W.=very weak.

TABLE III.—Alloy A (5 per cent. Mg).
(Face-centred cubic.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
* K_β	111	V.W.	4·186	4·043
* K_α	111	V.W.	4·029	4·043
K_β	111	M.	2·089	2·089
K_α	111	St.	2·098	2·098
L_α (tungsten) .	100 (2)	W.	1·820	1·817
K_α	100 (2)	St.	1·821	1·817
K_α	110 (2)	St.	1·283	1·284
L_α (tungsten) .	131	W.	1·093	1·096
K_α	131	St.	1·094	1·095

NOTE.—Lines of β phase are marked with an asterisk (*).

The copper lattice, whose dimensions have been determined frequently but not conclusively, was found to have the known face-centred structure with a base $a_0 = 3·610$ Å.U. The copper used was high-grade electrolytic metal of 99·88 per cent. purity, powdered by friction with emery-cloth and tested, as described in a previous section. The phase in which copper is the solvent has the same face-centred structure, but the lattice constant increases with increasing magnesium-content to a constant value about ·66 per cent. greater than that of pure copper.

TABLE IV.—Alloy B (11 per cent. Mg).
(Mixture of two face-centred cubic systems.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
* K_α	111	M.	4·047	4·043
* K_α	110 (2)	W.	2·481	2·476
* K_α	131	St.	2·112	2·112
* K_α	111 (2)	St.	2·024	2·022
K_α	100 (2)	M.	1·817	1·817
* K_α	100 (4)	M.	1·752	1·751
* K_α	331	M.	1·607	1·607
* K_α	112 (2)	W.	1·429	1·429
* K_α	151	St.	1·347	1·348
K_α	110 (2)	M.	1·283	1·285
* K_α	110 (4)	St.	1·237	1·238
* K_α	351	M.	1·183	1·184
K_α	131	M.	1·093	1·096
* K_α	253	M.	1·067	1·068
* K_α	131 (2)	M.	1·055	1·056
* K_α	111 (4)	W.	1·010	1·011
* K_α	155	W.	·9807	·9806
* K_α	371	St.	·9125	·9117
* K_α	100 (8)	M.	·8981	·8754

NOTE.—Lines of β phase are denoted by an asterisk (*).

Table III., for alloy A, gives the planar spacings due to such a lattice with base $a_0 = 3·634$ Å.U. This expansion of the unit cell is due to the substitution of the magnesium atoms with their larger atomic radii for some of the copper atoms in the copper lattice.

Two of the innermost lines of the β phase were also present on the photograph, very faintly, constituting evidence that copper holds less than 5 per cent. magnesium in solution at room temperature. The faintness of these lines shows that this composition (5 per cent. magnesium) is near to the limit of solution of magnesium in copper.

This limit may be estimated as falling at about 3 per cent. magnesium at room temperature.

TABLE V.—Alloy C (16 per cent. Mg).

(Face-centred cubic of spinelle type.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_β	111	W.	3·872	4·061
K_α	111	M.	4·066	4·061
K_α	110 (2)	W.	2·492	2·487
K_β	131	V.W.	2·115	2·121
K_β	111 (2)	V.W.	2·032	2·031
K_α	131	St.	2·125	2·121
K_α	111 (2)	St.	2·035	2·031
K_α	100 (4)	M.	1·761	1·759
K_α	331	M.	1·615	1·614
K_α	112 (2)	W.	1·434	1·436
K_α	151	St.	1·353	1·354
K_α	110 (4)	St.	1·243	1·243
K_α	351	M.	1·187	1·189
K_α	353	M.	1·068	1·072
K_α	131 (2)	M.	1·059	1·060
K_α	111 (4)	W.	1·015	1·015
K_α	155	W.	·9837	·9849
K_α	173	St.	·9157	·9157
K_α	100 (8)	M.	·9002	·8793

The photograph of B (Table IV.), showing the lines of the α and β phases, confirms the deductions from A. The lattice constant of the α phase from this photograph is $a = 3{\cdot}630$ Å.U., which is in good agreement with the previous result.

The β Phase.

The structure of the β phase, thought by Sahmen to be Cu_2Mg, has been obtained from a study of the photograph yielded by alloys B, C, and D. The data are given in Tables IV., V., and VI. The phase was found to have a face-centred structure with a lattice constant which varies from 7·003 to 7·059 Å.U.

TABLE VI.—Alloy D (25 per cent. Mg).
(Mixture of face-centred spinelle structure and hexagonal structure.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_α	10·0	V.W.	4·625	4·573
K_α	10·1	V.W.	4·413	4·436
* K_α	111 10·2	W.	4·084	4·076 4·089
K_α	10·3	V.W.	3·639	3·658
* K_α	110 (2) 11·2 10·6	V.W.	2·514	2·496 2·534 2·536
K_α	11·3	V.W.	2·408	2·423
K_α	00·1 (8) 10·7	M.	2·270	2·286 2·269
* L_α (tungsten)	131 11·5	V.W.	2·126	2·128 2·141
* K_α	131 11·5	St.	2·133	2·128 2·141
K_α	10·2 (2) 10·8 00·1 (9)	St.	2·042	2·045 2·032
K_α	10·9	V.W.	1·860	1·857
* K_α	100 (4)	M.	1·751	1·764
* K_α	12·4 331	M.	1·619	1·616 1·619
* K_α	151	M.	1·359	1·359
K_α	00·1 (4)	W.	1·308	1·306
* K_α	110 (4)	M.	1·247	1·247
* K_α	351	V.W.	1·193	1·193
K_α	00·1 (16)	V.W.	1·141	1·143
K_α	20·1 (2)	V.W.	1·134	1·134
* K_α	353	W.	1·074	1·076
* K_α	131 (2)	V.W.	1·064	1·064
* K_α	111 (4)	V.W.	1·018	1·018
* K_β	100 (8)	V.W.	·9064	·8824
* K_α	173	M.	·0918	·9190
* K_α	100 (8)	W.	·8835	·8824

NOTE.—Lines of the β phase are marked with an asterisk (*).

Friauf* has determined, by powder and Laue methods, the structure of a β-phase alloy said to be Cu_2Mg. This had a face-centred lattice with a base $a_0=6\cdot99$ Å.U., and an experimentally determined density of 5·85 requiring eight molecules in the unit cell. As a result of his work he deduced a structure for Cu_2Mg of the spinelle type, the magnesium and copper atoms having the same arrangement as the metallic atoms in that compound. The atoms of magnesium are arranged in the same manner as the carbon atoms in diamond. This leaves four small cubes, each one-eighth of the unit cell in volume, unoccupied by magnesium atoms. The sixteen copper atoms are disposed in these cubes four in each, symmetrically arranged at the mid-points of the semi-diagonals of each cube.

The results of the present investigation, begun in October 1927, corroborate Friauf's work as to the type, but not the dimensions of the structure. Alloy C has a composition within ·6 per cent. of that corresponding to Cu_2Mg (Table I.). Reflexions (Table V.) are present in the first order only from planes having all indices odd, indicating that the lattice is a face-centred one. Its dimensions are $a_0=7\cdot034$ Å.U., a difference of nearly 6 per cent., as compared with Friauf's value. Its density of 5·72 requires eight molecules in the unit cell.

The relative intensities of the lines of the powder photograph were calculated for the spinelle structure, making use of the expression given by Wyckoff † based on the assumption that the scattering power of the atom is proportional to the square of the atomic number.

Satisfactory agreement between the calculated and the observed intensities was obtained. Close agreement could not be expected, since the structure is a complicated one and the formula empirical.

In view of the results about to be detailed, it seems likely that the alloy investigated by Friauf did not have the composition Cu_2Mg, although it may have been homogeneous under the microscope. According to Sahmen's diagram, the β phase consists of pure Cu_2Mg only. The results of the present investigation do not confirm this. The lattice constant varies over a range of composition. The limits of the variation were determined from measurements on alloys B and D. A reference to Table I. and to fig. 3 shows that these two alloys fall, on the equilibrium diagram, B between the α and β phases, and D between the β and Mg_2Cu phases.

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* J. Am. Chem. Society, xlix. p. 3107 (Dec. 1927).

† 'The Structure of Crystals,' p. 107.

They should each, therefore, show the lines of two components —the photograph of B showing the lines of the α and the lower limits of the β phases, and that of D showing the lines of the higher limit of the β together with those of the Mg_2Cu phase. Such was found to be the case, and the structure limits of the β phase were thus determined. The measurements are given in Tables IV. and VI., and the resulting limits, as previously stated, are 7·003 Å.U. on the high copper-content side, and 7·059 Å.U. on the high magnesium-content side.

Cu_2Mg can, therefore, hold in solution both copper and magnesium, and the β phase must be a solid solution. Since films of both alloys B and D show the lines of two distinct phases, the limits of the solid solution must be between 89 and 75 per cent. copper. The lines of Mg_2Cu from alloy D are comparable in intensity with those of the β phase. Those of the α phase in the photograph from alloy B are very faint.

The limits of the β phase must therefore, on the one hand, be close to the composition of alloy B, and, on the other hand, be far removed from that of alloy D. It may be estimated that the β phase is confined to 2 or 3 per cent. on either side of the Cu_2Mg composition.

Friauf's value of 6·99 Å.U. for the lattice constant of the alloy examined by him is in close agreement with the value 7·003 Å.U. of the lower limit of the β phase. The density 5·85 of his alloy is that corresponding with a composition of 85·5 per cent. copper, according to the experimental density curve. The method of preparation of the alloy was that of melting together the calculated amounts of magnesium and copper in an electric furnace and allowing the melt to cool slowly. Under these conditions slight loss of magnesium is extremely likely to occur. It therefore seems probable that what he investigated was an alloy having a composition just on the lower limit of solution. If this is assumed, his results agree well with those given here, and the lower limit of the β solution is placed at 85·5 per cent. copper.

The lattice constant of alloy C is 7·034 Å.U. and the experimental density 5·72. The theoretical density, treating the alloy as a solid solution, is 5·76. The discrepancy is probably due to slight porosity of the material.

It is of interest to note that, as in the case of the α solution, no difference in the relative intensity of corresponding lines of the β solution may be detected in any of the photographs of B, C, and D—despite the changes in the dimensions of the structure due to solution.

The Mg_2Cu Phase.

The positions and relative intensities of the lines due to Mg_2Cu are the same, within experimental error, on all photographs in which they appear. Its crystal structure therefore remains unchanged in a series of alloys representing an extended range of composition.

The fundamental lattice, determined from measurements on the photographs obtained with alloy F (Table VIII.), was found to be hexagonal, with an axial ratio 3·464. The unit cell has a base of 5·281 Å.U. No reflexions are present which require a greater cell than this. The density 3·35 requires eight molecules in the unit cell. It is seen from Table VIII. that all lines on the film are satisfactorily accounted for by this structure.

The placing of the atoms within the cell is not possible from powder data alone, and additional measurements on single crystals are required to render the treatment complete.

Measurements on the films for alloys D and E corroborate the equilibrium diagram in that the lines of both β and Mg_2Cu phases are present on the same film. Analysis of these films was rather difficult as several lines of the two phases coincide. This was to be expected as both phases are built up of the same two kinds of atoms. Considerations of atomic radius would therefore lead one to expect that certain planes of both phases would have the same spacing. A careful examination of the film leads to the separation of the two sets of lines. This is facilitated by the fact that in the D photograph the β lines are most intense, while in that of E the Mg_2Cu predominate. Alloy E (Table VII.) gives a β lattice with $A_0 = 7{\cdot}066$ Å.U. and an Mg_2Cu lattice of base 5·276 Å.U. The corresponding figures for the D alloy are 7·059 and 5·288 Å.U., which agree within the limits of accuracy of the measurements.

Magnesium.

The structure of magnesium has been shown by previous researches * to be close-packed hexagonal, with axial ratio 1·624. Table XI. gives measurements on the magnesium films corroborating this result and giving a base of length 3·206 Å.U., slightly smaller than the previously-accepted value of 3·22 Å.U.

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* A. W. Hall, Proc. Nat. Acad. Soc. iii. p. 470; Owen & Preston, Proc. Phys. Soc. xxxv. p. 101.

TABLE VII.—Alloy E (36 per cent. Mg).

(Mixture of spinelle structure and hexagonal structure.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_a	10·0	M.	4·601	4·573
K_a	10·1	M.	4·441	4·436
K_a	10·2	M.	4·097	4·090
K_a	10·3	M.	3·663	3·658
K_a	10·6 11·2	M.	2·544	2·536 2·534
K_a	11·3	M.	2·312	2·423
K_a	00·1 (8) 10·7	St.	2·282	2·286 2·269
* K_a	11·5 131	St.	2·137	2·141 2·128
* K_a	10·8 00·1 (9) 111 (2)	St.	2·042	2·045 2·032 2·038
K_a	10·9	W.	1·857	1·857
* K_a	100 (4)	V.W.	1·769	1·765
K_a	12·1	V.W.	1·714	1·698 1·721
* K_a	12·4 331	W.	1·620	1·616 1·619
K_a	12·5	V.W.	1·561	1·562
K_a	10·1 (3)	V.W.	1·474	1·478
K_a	12·7	M.	1·438	1·441
K_a	11·11	M.	1·406	1·407
* K_a	151 10·2 (3)	M.	1·361	1·358 1·363
K_a	30·7	M.	1·312	1·316
K_a	10·6 (2) 11·2 (2)	V.W.	1·268	1·268 1·267
K_a	110 (4)	M.	1·250	1·248
K_a	12·11	W.	1·195	1·198
K_a	22·7	V.W.	1·180	1·178
K_a	20·1 (2)	M.	1·138	1·343
K_a	30·11	V.W.	1·121	1·124
K_a	11·15	W.	1·106	1·107
* K_a	353	V.W.	1·077	1·077
* K_a	131 (2)	M.	1·065	1·064
* K_a	111 (4)	W.	1·019	1·019

NOTE.—Lines which include the β phase are marked with an asterisk (*).

TABLE VIII.—Alloy F (47 per cent. Mg).

(Hexagonal structure: $a = 5{\cdot}281$ Å.U. axial ratio $= 3{\cdot}464$.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_a	10·0 00·1 (4)	M.	4·585	4·513
K_a	10·1	M.	4·420	4·436
K_a	10·2	V.W.	4·096	4·090
L_a (tungsten)	10·3 00·1 (5)	V.W.	3·667	3·658
K_a	10·3 00·1 (5)	M.	3·658	3·658
K_a	10·6 11·2	M.	2·537	2·536 2·533
K_a	11·3	M.	2·410	2·422
K_a	10·7 20·1	St.	2·276	2·269
K_a	11·5 20·3	M.	2·137	2·140
K_a	10·2 (2) 00·1 (9)	St.	2·037	2·045 2·032
K_a	11·7 10·9	M.	1·858	1·857
K_a	12·1 20·7	V.W.	1·713	1·720 1·698
K_a	12·4 10·4 (2)	W.	1·616	1·616
K_a	12·5 10·11	M.	1·565	1·563
K_a	12·6 11·10	V.W.	1·498	1·504
K_a	10·1 (3)	W.	1·478	1·478
K_a	12·7	M.	1·438	1·441
K_a	10·5 (2)	M.	1·433	1·428
K_a	30·5 11·11 00·1 (13)	M.	1·406	1·407
K_a	10·2 (3)	V.W.	1·364	1·363
K_a	10·13 20·11	V.W.	1·346	1·345
K_a	30·7	St.	1·315	1·316
K_a	00·1 (14)	St.	1·307	1·306
K_a	10·6 (2) 11·2 (2)	V.W.	1·266	1·268 1·266
K_a	12·11	V.W.	1·195	1·196

TABLE VIII. (*cont.*)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_{α}	22·7 10·15	V.W.	1·180	1·178
K_{α}	30·10 31·6	V.W.	1·168	1·170
K_{α}	10·7 (2) 20·1 (2)	M.	1·136	1·134
K_{α}	30·11 40·3	W.	1·119	1·123
K_{α}	11·15	W.	1·106	1·107

TABLE IX.—Alloy G (54 per cent. Mg).

(Mixture of two hexagonal structures.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated
K_{β}	10·1	V.W.	4·421	4·436
K_{α}	10·0	M.	4·593	4·573
K_{α}	10·1	M.	4·434	4·436
K_{α}	10·2	V.W.	4·066	4·089
K_{α}	10·3	M.	3·658	3·658
* K_{α}	10·0	W.	2·779	2·777
* K_{α}	00·1 (2)	W.	2·611	2·603
* K_{α}	10·1	M.	2·452	2·450
K_{α}	11·3	M.	2·406	2·422
K_{α}	00·1 (8) 10·7	St.	2·278	2·286 2·269
K_{α}	10·2 (2) 00·1 (9)	St.	2·039	2·045 2·032
* K_{α}	10·2	W.	1·898	1·899
K_{α}	10·9	M.	1·856	1·857
* K_{α}	11·0	W.	1·604	1·603
K_{α}	12·5	M.	1·564	1·563
* K_{α}	10·3	W.	1·471	1·472
K_{α}	12·7	M.	1·438	1·441
K_{α}	11·11	M.	1·403	1·406
K_{α}	10·2 (3)	W.	1·363	1·363
K_{α}	10·13	W.	1·340	1·344
K_{α}	30·7	M.	1·315	1·316
K_{α}	22·7	V.W.	1·179	1·178

NOTE.—Magnesium lines are denoted by an asterisk (*).

TABLE X.—Alloy H (82 per cent. Mg).
(Mixture of two hexagonal structures.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_β	10·1	W.	4·383	4·436
K_α	10·0	W.	4·593	4·573
K_α	10·1	W.	4·436	4·436
K_α	10·3	W.	3·663	3·658
* K_β	00·1 (2)	W.	2·593	2·603
* K_α	10·0	M.	2·785	2·776
* K_β	10·1	W.	2·424	2·449
* K_α	00·1 (2)	M.	2·608	2·603
K_α	10·6 11·2	W.	2·532	2·536 2·533
* K_α	10·1	St.	2·454	2·450
K_α	00·1 (8) 10·7	M.	2·278	2·286 2·268
K_α	11·5	V.W.	2·138	2·140
K_α	10·2 (2) 00·1 (9)	M.	2·039	2·045 2·032
* K_α	10·2	M.	1·899	1·899
* K_α	11·0	M.	1·604	1·603
K_α	12·5	V.W.	1·567	1·562
* K_α	10·3	M.	1·471	1·471
* K_α	10·0 (2)	V.W.	1·387	1·388
* K_α	10·2 (3) 11·2	M.	1·363	1·363 1·365
* K_α	20·1	M.	1·340	1·341
* K_α	00·1 (4)	W.	1·300	1·301
* K_α	10·1 (2)	W.	1·223	1·224
* K_α	10·4	W.	1·176	1·178
* K_α	20·3	W.	1·082	1·084
* K_α	12·1	W.	1·027	1·028
* K_α	11·4	W.	1·009	1·010
* K_α	10·5	W.	·9740	·9749
* K_α	12·3	W.	·8977	·8980

NOTE.—Magnesium lines are denoted by an asterisk (*).

The measurements for alloys G and H are given in Tables IX. and X. In both, the lines due to Mg_2Cu and magnesium appear having the same positions, within experimental error, as in the pure components.

As previously remarked, the variation of the dimensions of the magnesium lattice in these films is one in 3200. That of the Mg_2Cu lattice is one in 5280. The relative intensities of the lines also remain the same. If, therefore, there is any solution of magnesium in Mg_2Cu, and of copper in magnesium, the amount is so small as to be undetected by present methods.

The results of the present investigation, and, in particular, of the section dealing with the β phase, demonstrate the necessity for a thorough quantitative exploration of a system before the structure of any isolated phase may be determined with full knowledge of all the factors concerned. The simplicity of an equilibrium diagram obtained by metallurgical methods may not be trusted implicitly in such cases. A survey by X-ray analysis of the region on either side of the particular composition to be examined is therefore of primary importance to form the basis of a satisfactory investigation.

Table XI.—Magnesium.

(Hexagonal closed packed.)

Radiation.	*h k l.*	Intensity.	*d/n* observed.	*d/n* calculated.
K_a …………	10·0	M.	2·785	2·777
K_a …………	00·1 (2)	M.	2·608	2·603
K_a …………	10·1	St.	2·454	2·450
K_a …………	10·2	M.	1·899	1·899
K_a …………	11·0	M.	1·603	1·603
K_a …………	10·3	M.	1·471	1·471
K_a …………	11·2	M.	1·364	1·365
K_a …………	20·1	M.	1·341	1·341
K_a …………	20·3	W.	1·081	1·084
K_a …………	12·1	W.	1·028	1·029
K_a …………	11·4	W.	1·010	1·011
K_a …………	12·2	W.	·9741	·9750
K_a …………	12·3	W.	·8980	·8980
K_a …………	30·2	V.W.	·8727	·8678

SUMMARY.

The copper-magnesium system of alloys has been investigated by the X-ray powder method.

Eight alloys were prepared, and their compositions were

determined by an electrolytic method—their densities by the suspension method.

X-ray powder photographs of each alloy were taken, and, with the procedure adopted, an accuracy of measurement of one in six hundred was obtainable.

The equilibrium diagram, due to Sahmen, was confirmed in its main features. Two new regions of solid solution were detected, viz.:—

(i.) The α phase—a solution of magnesium in the copper lattice up to approximately 3 per cent. magnesium.

(ii.) The β phase—a range of solution extending on either side of the composition represented by the formula Cu_2Mg. It is estimated that the β phase is confined to 2 or 3 per cent. on either side of the Cu_2Mg composition.

The α phase has a face-centred structure with a base varying from 3·610 Å.U. in copper to 3·634 Å.U. at the limit of solution.

The β phase has the face-centred spinelle structure, with eight molecules in the unit cell and having a base varying from 7·003 Å.U. to 7·059 Å.U., the dimensions increasing with increasing proportion of magnesium.

The Mg_2Cu phase was found to possess a hexagonal lattice of unvarying dimensions. The unit cell contains eight molecules with $a_0=5{\cdot}281$ Å.U. and an axial ratio 3·464. In all other details Sahmen's diagram was verified. No trace of solid solution could be detected at the maximum end of the diagram.

The lattice constants of copper and magnesium were found to be copper $a_0=3{\cdot}610$ Å.U. and magnesium $a_0=3{\cdot}206$ Å.U. with axial ratio 1·624.

In conclusion, our thanks are due to Professors E. J. Evans and C. A. Edwards for facilities placed at our disposal for carrying out this research. We are also under obligation to Mr. Allen and Professor Taverner, of the Metallurgical Department, for advice and assistance in the preparation of the alloys.

APPENDIX.

Since the foregoing was written a publication on the copper-magnesium system by Westgren and his co-workers[*] has appeared.

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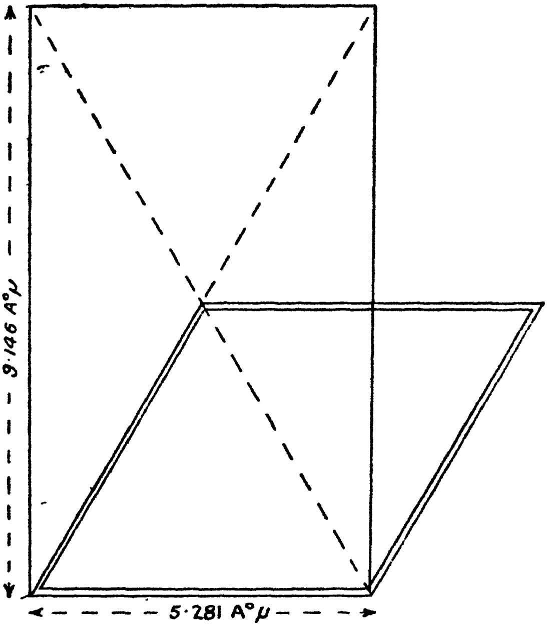
[*] *Zeit. Anorg. Chem.* Bd. clxxv. Heft 1–3 (1928).

The results of these authors are in general agreement with those described here, except apparently in the case of the crystal structure of Mg_2Cu. They found an orthorhombic arrangement of atoms for this alloy with a unit cell of edges $a_1=5{\cdot}273$ Å., $a_2=9{\cdot}051$ Å., and $a_3=18{\cdot}21$ Å. containing 16 molecules.

In the present investigation a hexagonal structure with unit cell of base 5·281 Å. and height 18·29 Å. was deduced containing eight molecules. A closer inspection reveals that the difference is one of the choice of axes. An orthorhombic cell of the above dimensions can be referred to hexagonal axes. If this is done, then the semi-diagonal of the base of the orthorhombic cell becomes a side of the base of the unit prism of the hexagonal arrangement (see fig. 4), giving a unit cell of one-half the volume of the first. The height is the same in both cases.

Fig. 4.



Mg_2Cu. Base of unit cell.
Single lines—Orthohrombic structure.
Double lines—Hexagonal structure.
Height is the same in both cases, 18·29 A.U.

CXXVII. *The Frequency-Distribution of Examination Marks.*

By W. N. Bond, *M.A.*, *D.Sc.*, *F.Inst.P.*, *Lecturer in Physics in the University of Reading* *.

Summary.

It is shown that the frequency-distribution curves of the marks awarded to candidates in non-competitive examinations should not be of various extreme types if it is desired to arrange all the candidates so as to represent their order of merit and relative merit accurately. This implies that there is likely to be an optimum form of frequency-distribution curve, which the examiners should use their control to endeavour to obtain. A comparison of curves obtained in various examinations gives evidence that there is considerable consensus of opinion as to the desirable form of curve. It is shown that the mean curve deduced from these examinations approximates closely to a curve of simple mathematical form, which has probably more significance than a mere average.

THE frequency-distribution of the marks awarded to candidates in an examination is influenced by the range of attainment of the candidates, by the range of difficulty and type of the questions, by the method of marking, and by various kinds of error †. The frequency-distribution curve is therefore partly, but not completely, under the examiners' control.

If the range of questions is much wider than is required to test the range of candidates concerned, the curve will in general consist of an isolated hump at some point in the range of marks attainable. This hump will usually be sensibly symmetrical and of the normal Gauss's form ‡. The shape of the hump is here primarily influenced by the relative attainments of the candidates; the curve is rather analogous to that for a physical characteristic of the candidates, such as their height. The marks awarded in such an examination would appear to represent the relative merits of the candidates in the subject concerned, the per cent. mark at which the peak occurs having no absolute significance; but the result will be influenced by the errors of marking etc.

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* Communicated by the Author.

† Edgeworth, Journ. Statistical Soc. 1888.

‡ Journ. Indian Math. Soc., April 1922; Encyc. and Dict. of Education, iv. p. 1593 (1922).

The maximum attainable mark being finite (say 100), the above type of examination would result, in an extreme case, in all the candidates receiving the same or almost the same mark. To avoid this defect it is therefore necessary to have a less wide range of questions. In fact it is desirable that every mark between 0 and 100 may at times be attained by some candidate. However, except for this broadening of the hump of the curve, the curve should be as nearly as possible unchanged in shape (so that the marks may still nearly represent the relative merit of the candidates, and not only their order of merit) *. The curve should therefore be, as a rule, nearly symmetrical about the 50-per-cent. mark. (In competitive examinations the better candidates may be arranged in order of merit more accurately by having the average mark attained less than 50 per cent., but this gives less accuracy in the ordering of the less successful candidates, and also makes the marks less representative of the relative merit of the candidates.)

Though it is advocated that the range of questions should not be too great for the range of capability of the candidates, on the other hand it is also necessary that the range of questions shall not be too limited in relation to the range of candidates. Thus, if the whole of a school were examined by questions of a standard suitable for a middle form (or if the highest form were examined entirely by questions of one type, such as problems in permutations and combinations), a double-humped curve might frequently result. The marks would then not represent the relative merit of the candidates, and would only facilitate the accurate placing of the medium candidates in order of merit.

With the curve thus limited (being approximately symmetrical, with a single hump somewhat like that of a normal Gauss's form and with a standard deviation that is neither too small nor too large), it appears likely that there is an optimum form of curve. At this stage we may consider the curves actually obtained in certain examinations. It is found † that in the subjects in which the marking is fairly determinate the different curves differ little, but that in the subjects in which "taste" affects the number of marks awarded, the curves have a smaller standard deviation and also differ appreciably from one another. For the purposes of the present investigation, data were collected for ten cases

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* Not as advocated by B. C. Wallis (see 'Nature,' Dec. 29, 1928, p. 1013).

† Crofts and Jones, 'Secondary School Exam. Statistics,' pp. 51-2 (1928).

of subjects of the more determinate type. At least seven of these sets could be considered quite independent; and the cases were chosen where the average number of marks attained by a candidate was very nearly 50 per cent. School and University examinations were included, and the subjects comprised Elementary English and Arithmetic, Mathematics, Physics, Science subjects, Agriculture and Commerce. Equal "weight" was given to each of the ten sets. The mean values so deduced are given in the second line of Table I., and the individual sets are illustrated in the figure, in which the crosses correspond to the mean values. (In the figure the average value of the probability in each interval is plotted.)

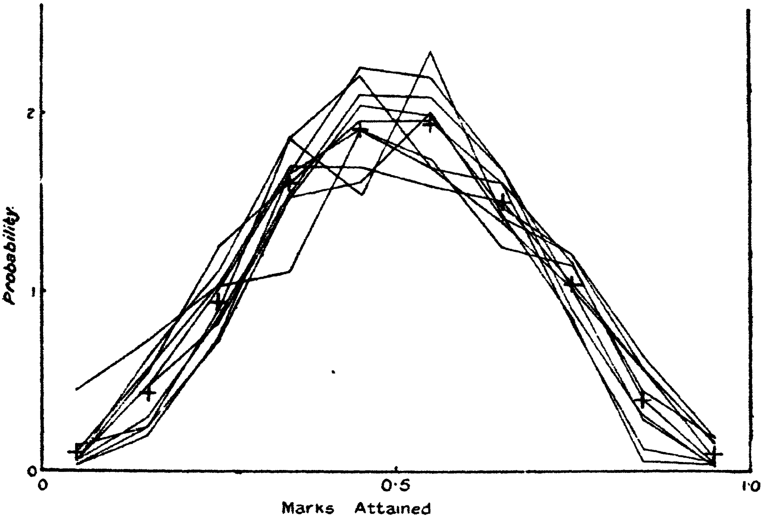

TABLE I.

Per cent. marks:—	0–9.	10–19.	20–29.	30–39.	40–49.	50–59.	60–69.	70–79.	80–89.	90–100.
Percentage of candidates:—										
Observed:	1·0 ±0·2	4·3 ±0·4	9·4 ±0·5	16·1 ±0·4	19·1 ±0·5	19·4 ±0·5	15·1 ±0·4	10·5 ±0·4	4·0 ±0·5	1·0 ±0·2
Equation 1:	0·6	4·3	10·0	15·7	19·4	19·4	15·7	10·0	4·3	0·6
Equation 3:	1·0	4·5	9·9	15·5	19·1	19·1	15·5	9·9	4·5	1·0

Denoting the range of marks attainable by $x=0$ to $x=1$, for convenience, the peak of the curve at $x=0{\cdot}5$ is found by interpolation to have a height $y=1{\cdot}98\pm0{\cdot}035$. The height of the peak in the corresponding determinate subjects given by Crofts and Jones* I estimate as $2{\cdot}00\pm0{\cdot}03$ (but the maximum is at about 45 per cent. marks).

These results show a considerable consensus of opinion, and also indicate that the curve is of simple form, as its maximum height is $1{\cdot}99\pm0{\cdot}03$. The curve is to a first approximation a triangle ; to a second approximation it may be represented by the equation :

$$y=2\sin^2\pi x. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values deduced from this equation are given in Table I. From the beginning it had been decided to compare the observed value with an extension of the "binomial" or "law of large numbers" form of curve. It was hoped that, not only might this law be found to represent the data satisfactorily, but also that the adjustable constants might be found to approximate to simple values. We may thus replace the binomial series of ordinates by a continuous curve :

$$y=\mathrm{A}\,.\,(n+2)\frac{\Gamma(n+2)}{\Gamma(\overline{n+2}\,.\,x)\,.\,\Gamma(\overline{n+2}\,.\,\overline{1-x})}$$
$$\times\, a^{(n+2)x-1}\,.\,(1-a)^{(n+2)(1-x)-1} \quad . \quad (2)$$

In the present case $a=0{\cdot}5$ by symmetry, n is found to be 2 (within the error of observation), and to make the area unity this requires $\mathrm{A}=0{\cdot}98_7$. The equation then reduces to

$$y=\frac{1{\cdot}97_5}{\Gamma(4x)\,.\,\Gamma(4\,.\,\overline{1-x})}, \quad . \quad . \quad . \quad . \quad (3)$$

The results deduced from this equation are given in Table I. Equations (1) and (3) both fit the observations within the errors of observation. Prof. Pearson's Type IV. curve can be used to obtain about as good a fit, but is definitely empirical.

Whether either of equations (1) and (3) represents more than an empirical law or not, it appears likely that the observed values are approximating closely to a fundamental, simple, and fixed curve—which is the ideal to aim at in most examinations. Equations (1) and (3) represent smooth curves drawn through a set of equidistant ordinates that are proportional to 0, 1, 2, 1, 0, the area under the curve being unity; the peak heights are 2·00 and $1{\cdot}97_5$ respectively.

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* *Loc. cit.*

I should like to thank Prof. J. A. Crowther and Miss I. E. Campbell for help in obtaining some of the data, and to say that this work was induced by that given in an earlier paper ("The Magnitude of Non-Dimensional Constants," Phil. Mag., April 1929).

Department of Physics,
University of Reading,
April 6th, 1929.

CXXVIII. *Has the Temperature of Radiation any Effect on its Photographic Action?* *By* Dr. R. A. Houstoun, *Lecturer on Physical Optics in the University of Glasgow* *.

It is well known that when radiation is in equilibrium with matter in a cylinder it has the temperature of that matter. This is assumed in the proof of the Stefan-Boltzmann law of radiation and also in the proof of Wien's displacement law. If a hole is pierced in the cylinder, the radiation which issues has the same temperature which it had inside.

The temperature of a beam is not a property to which the experimental physicist has hitherto devoted attention, because he has regarded it as belonging rather to the source than to the beam itself. Planck, however, points out † that we distinguish between the "black body temperature" of the sun and its real temperature, and that the "black body temperature" of the sun, being the temperature of a black body emitting the same radiation as the sun, is a property of the radiation emitted and not of the sun at all; consequently, it is more sensible to speak of the sun emitting radiation which possesses a temperature of so many degrees.

If we accept the principle of relativity, radiation has more "substance" than the space in which it is propagated, and it becomes easy to imagine its having temperature. We can then think with Planck of a point in space crossed by different beams of light each possessing its own temperature; even the different colours in the same beam may have different temperatures. And the medium through which the radiations are propagated may have a temperature quite different from any of them.

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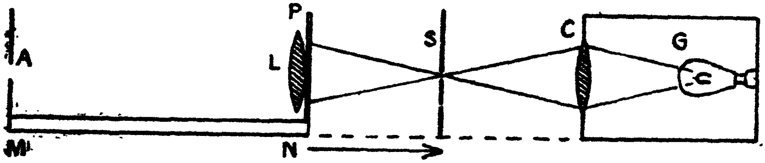
* Communicated by the Author.

† 'Theory of Radiation,' § 101.

It occurred to me that the ability of a radiation to ionize a molecule or atom might depend on its temperature. The simplest way of putting the matter to test appeared to be to deliver two quantities of light of the same energy-content but different temperatures in the same time on equal adjacent areas of the same photographic plate. Photographic action is essentially a case of ionization. Of course the density of the photographic image has been regarded hitherto as due wholly to the intensity of the radiation and the time it acts, but an effect of temperature was never specifically looked for.

The figure represents the arrangement I have employed to carry out the test. The source of light was a 40-watt gas-filled lamp which was run off the 250-volt lighting circuit in series with a rheostat and milliammeter. The lamp was enclosed in a light-tight box. A lens in one side of the box focussed the filament on a hole in a brass plate S. The diameter of this hole was either 4 mm. or 1·62 mm., so that only a small portion of the image was able to pass through. The rays diverged from the hole and fell on a ground-glass plate P, behind which was a lens L. The ground side of the glass was towards the lens. Both ground glass and lens were mounted at one end of a wooden base MN which could be moved up towards S. At the other end was fixed an aperture, exactly at the focus of the lens. Immediately behind this aperture was placed the photographic plate.



The lens was a biconvex one of focal length 27·9 cm., the radius of curvature being 28·16 cm. Hence its index of refraction was 1·5046. The distance through which MN was displaced was 16·7 cm. The diameter of the luminous disk on the ground glass PN was 5·8 cm.

Since the aperture A is at the focus of the lens, all the rays which are scattered in a direction parallel to the axis of the system arrive at A. Now suppose that the base MN moves up in the direction of the arrow towards S. The luminous disk in which the cone meets the plate contracts to a point. After the displacement exactly the same quantity of light is scattered in a direction parallel to the axis of the system as before, and this light is brought to a focus by the lens at A. The base MN, it should be mentioned, ran along a guide from the one position to the other, and was on a different table from the lamp and screen S for fear that S might be disturbed by its motion. Thus in the one position the light came to A from a disk of diameter 5·8 cm.; in the other position the light came to A from a point or rather an extremely small area. In this second case, since the source appeared much brighter to an eye situated at A, it was emitting light of a higher temperature.

The distinction may be put in another way. In the first case a wide angle beam falls on the photographic plate; in the second case a narrow angle beam delivers the same quantity of energy in the same time on the plate. The change of angle involves at the same time a change in the profile of the wave-train, and I thought that this change of profile might be of decisive importance for ionization.

The statement that the same quantity of energy falls on A in the two cases requires slight corrections. Until the rays fall on the lens L, the losses are the same, but the high temperature light goes through a thicker part of the lens and falls on its surfaces and the surface of the photographic plate at A more normally.

The magnitude of these corrections can easily be calculated. The difference in the thickness of glass passed through is 0·03 cm. But according to W. D. Haigh* optical glass of the same refractive index as the lens used absorbs about 2 per cent. of the incident light per inch. Hence the correction due to different absorption in the glass is negligible.

The extreme ray of the wide angle pencil falls on the photographic plate at 6° with the normal. Fresnel's reflexion coefficients for this angle in the case of a medium of refractive index 1·5 are 0·2009 for the ray polarized in the plane of incidence, and 0·1981 for the ray polarized at right angles to the plane of incidence. The value for normal incidence is in each case 0·20000. Hence the difference is too small to affect the result. The difference will be smaller still in the case of the reflexion losses at the surfaces of the lens, for the angles of incidence are less there. Consequently, we can ignore them and assume that both beams eliver the same content of energy.

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* Proc. Opt. Conv. 1926, p. 327.

The following table gives the details of the experiments made :—

List of Experiments.

Name of Plate.	Exposure.	° K.	° K.
Paget Slow Lantern	1 hour	1177	2000
	5 hours	1177	1850
Imperial Process	6 hours	970	1470
	17½ hours	970	1290
Wellington Ortho Process	10 min.	970	1470
	20 min.	1053	1560
	¾ hour	1177	1850
Imperial Special Sensitive	15 min.	1053	1670
	80 min,	1053	1560
Ilford Isozenith	10 min.	970	1470
	2 hours	970	1290
Imperial Panchromatic Process	30 min. red	970	1290
	17½ hours green	970	1290
	10 min. red	970	1470
	20 min. green	1053	1670
Ilford Special Rapid Panchromatic	5 min. red	970	1290
	1 hour green	1053	1560
	1 min. red	970	1470
	8 min. green	1053	1670

The temperatures are those of the two radiations under comparison. They are in degrees Kelvin. The words red and green mean that in these cases either the Wratten standard tricolour red or green filter was placed in the path of the rays between the lens C and the aperture S.

The results of the experiments were wholly negative. There was a slight difference on two of the plates, but this was traced to a variation of the voltage during the experiment. As a rule a difference in density of 5 per cent. could have been detected. The plate-holder had an arrangement for exposing first one rectangle and then another rectangle alongside it, which was difficult to work. So sometimes the rectangles made good contact and sometimes they did not.

The temperatures were obtained from Wien's radiation formula

$$S = c_1 \lambda^{-5} e^{-c_2/\lambda T}.$$

If we confine ourselves to one wave-length, this gives

$$\log S/S_0 = \frac{c_2}{\lambda}\left(\frac{1}{T_0} - \frac{1}{T}\right).$$

Hence, if the ratio of the radiation is known for two temperatures, and one of these temperatures is known, the other can be determined by means of the formula. It was assumed that, when the current through the lamp was diminished until the disk was just visible, the temperature of the radiation from the disk was 525° C. and the other temperatures calculated from this. They are, of course, only rough estimates. The ratio of the areas of disk and point was either about 1320 or about 3300.

There does not seem to be any method of greatly increasing the sensitiveness of the test.

CXXIX. *Heat Flow when the Boundary Condition is Newtons's Law.* *By* J. H. Awbery, *B.A.*, *B.Sc.*, *Physics Department, The National Physical Laboratory, Teddington, Middlesex* *.

Abstract.

The general problem of a body from which the heat loss at one or more surfaces is proportional to the excess temperature at the point, over that of the air, is considered with reference to those cases where the final steady state is not one of uniform temperature.

Two illustrative cases are worked out :—

(41) The case of a cable buried in the ground.

(42) The case of a conducting girder projecting into a layer of insulation.

1. *Introduction.*

The standard text-books on heat conduction usually consider one or two problems of the cooling of bodies under the condition that the heat loss from the surface is proportional to the temperature at the point considered; attention seems to be restricted, however, to problems of variable temperature, in which the initial state is given, and the final state is one of uniform temperature throughout.

It is the object of the present paper to consider the class of problems where there is a constant supply of heat at some point, line, or surface, so that the steady state reached is one in which there is a definite temperature distribution, other than a uniform distribution of heat.

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* Communicated by the Author.

2. *General Considerations.*

To each such problem corresponds another in which the boundary condition is replaced by the simpler one of an isothermal surface. If the latter problem is directly soluble by Fourier analysis, then the original one will, in general, be soluble by the same method, so that we need devote no attention to the case.

Consider, however, a problem where the solution of the corresponding isothermal case has been obtained by images, or conjugate functions, or some other method, with the result

$$v_1 = f(x, y, z),$$

where v_1 is the temperature at any point, when the isothermal boundary condition applies.

If we form the expression

$$v = v_1 + v_2,$$

where v_2 satisfies

$$\nabla^2 v_2 = 0,$$

everywhere except possibly at the heat source, v will satisfy the Laplace equation. Moreover, at the boundary under consideration v_1 has been constructed to vanish, so that v reduces to v_2, and the heat flow at this boundary to

$$-\mathrm{K}\frac{\partial v}{\partial n} \equiv -\mathrm{K}\left(\frac{\partial v_1}{\partial n} + \frac{\partial v_2}{\partial n}\right),$$

where n represents the outward-drawn normal to the boundary, and K is the thermal conductivity of the medium.

The expression of Newton's law is

$$\mathrm{E}v = -\mathrm{K}\,\partial v/\partial n,$$

so that the boundary condition reduces to

$$-\mathrm{K}\left(\frac{\partial v_1}{\partial n} + \frac{\partial v_2}{\partial n}\right) = \mathrm{E}v_2. \quad . \quad . \quad . \quad . \quad (1)$$

The first term is known, since v_1 is a known function of position, so that equation (1) is a differential equation, imposing a condition on v_2. If the physical problem is a definite one, the equations of type (1), at all the boundaries, together with the fact that v_2 is harmonic, are clearly sufficient to define v_2. (It may happen, however, that the condition at some boundaries will be Newton's law, and at others the isothermal condition will hold. This involves no extra difficulty.)

In general, the method of conjugate functions will not determine v_1 in the form postulated above (*i. e.*, as an explicit function of position). It is essentially a method for use in two dimensions, and it gives an equation of the form

$$w_1 = f(z), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $w_1=v_1+iu_1$, $z=x+iy$, and $u_1=k$ is the equation to the orthogonal surfaces of v_1, whilst $i=\sqrt{-1}$. (z is to be distinguished from the z previously used.) In this case the boundary condition remains of the form (1), but v_1 has now to be evaluated from the equation (2) before it can be substituted in (1). If we restrict consideration to the case where the boundary concerned is straight, the axes can always be selected so that this boundary becomes the line $y=0$. Then, since $w_1=f(z)$, the quantity to be evaluated is $\left(\frac{\partial v_1}{\partial y}\right)_{y=0}$. Even if the relation (2) cannot be separated into two equations, this evaluation can frequently be carried out; for differentiating the implicit equation (2), setting $dx=0$ and $y=0$, the value of $\partial w_1/\partial y$ is obtained. But

$$w_1 = u_1 + iv_1,$$

so that

$$\frac{\partial w_1}{\partial y_1} = \frac{\partial u_1}{\partial y_1} + i\frac{\partial v_1}{\partial y_1}$$

and the quantity required is the imaginary part of $\partial w_1/\partial y_1$, which will be of a simpler form than the original equation.

One case requires particular notice. The function to be taken in (2), to solve a given problem by the method of conjugate functions is frequently found by transferring the boundary on to the real axis of a subsidiary t plane. In these cases the equation (2) is replaced by

$$\left.\begin{aligned} w &= \mathrm{F}(t) \\ z &= \mathrm{G}(t) \end{aligned}\right\}, \text{ where F and G are known functions.}$$

It does not appear that the generalization from the isothermal to the Newton's law problem can be carried out in practice, in this case, unless t can be eliminated from the above pair of equations.

We propose to illustrate the method by working out two cases which present themselves in practice.

(1) A cable is buried in the ground, the heat loss from the latter being given by Newton's law. Mathematically

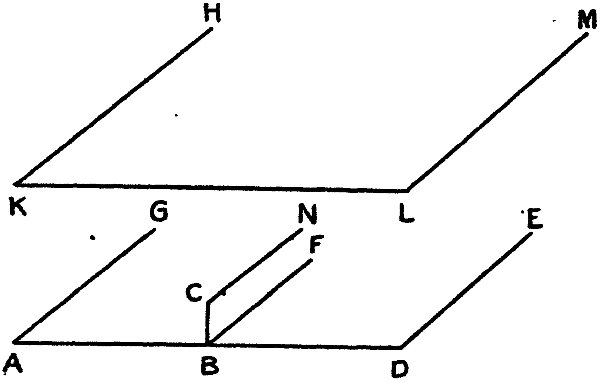
we shall represent this problem by that of a line-source in a semi-infinite medium, with one plane face to which the line-source is parallel.

(2) The case of a girder projecting into insulation. This is shown in fig. 1. We take the plane GADE, and the girder NCBF, as being rigorously at one and the same temperature; whilst the plane HKLM is the one from which heat loss is governed by Newton's law. Both planes extend to infinity in all directions, and the intervening space is filled with a homogeneous conducting medium.

3. *Example* I.—*Cable buried in the Ground.*

The solution of the corresponding problem when the ground is an isothermal at temperature v_0 is easily obtained by the method of images. Taking the surface of the ground as the plane $y=0$, and taking the plane $x=0$ as the perpendicular to the ground through the cable, the temperature at (x, y) is

Fig. 1.



$$v_1 = v_0 + \frac{Q}{4\pi K} \log\left(\frac{x^2 + \overline{y-a}^2}{x^2 + \overline{y+a}^2}\right),$$

where Q is the heat generation per second per cm. length of the cable, K is the thermal conductivity of the ground, and a is the depth of the cable below the surface.

For the case to be investigated, we take then

$$v = \frac{Q}{4\pi K} \log\left(\frac{x^2 + \overline{y-a}^2}{x^2 + \overline{y+a}^2}\right) + v_2,$$

where v_2 is harmonic, and v_0 has been taken as 0, which merely involves a change in the origin for temperature measurements.

In Cartesian coordinates a known solution of $\nabla^2 v_2=0$ is

$$v_2 = (\alpha e^{ny} + \beta e^{-ny})(\gamma \cos nx + \delta \sin nx),$$

and to avoid infinite temperatures as the depth increases, we must take $\beta=0$. We shall also find that the term in $\sin nx$ is unnecessary, so that we adopt $\mathrm{A}e^{ny}\cos nx$ as our fundamental solution. The limit of a series of such terms is

$$v_2 = \int_0^\infty \mathrm{A}e^{\lambda y} \cos \lambda x \, d\lambda,$$

which satisfies $\nabla^2 v_2=0$ and does not become infinite within the region we consider $(-\infty < y < 0)$.

Consequently, the problem will be solved if we take

$$v = \frac{\mathrm{Q}}{4\pi\mathrm{K}} \log\left(\frac{x^2+\overline{y-a}^2}{x^2+\overline{y+a}^2}\right) + \int_0^\infty \mathrm{A}e^{\lambda y} \cos \lambda x \, d\lambda \qquad \text{(IV.)}$$

with a suitable value of A.

When $y=0$, this becomes

$$v = \int_0^\infty \mathrm{A} \cos \lambda x \, d\lambda,$$

whilst $(\partial v/\partial y)_{y=0}$ is

$$-\frac{a\mathrm{Q}}{\pi\mathrm{K}(x^2+a^2)} + \int_0^\infty \mathrm{A}\lambda \cos \lambda x \, d\lambda.$$

The boundary condition $-\mathrm{K}\,\partial v/\partial y = \mathrm{E}v$ will thus be satisfied if

$$\int_0^\infty (\mathrm{E}+\mathrm{K}\lambda)\mathrm{A} \cos \lambda z \, d\lambda = \frac{a\mathrm{Q}}{\pi(x^2+a^2)}. \quad . \quad . \qquad \text{(V.)}$$

Now by Fourier's Integral Theorem,

$$\frac{a\mathrm{Q}}{\pi(x^2+a^2)} = \frac{2}{\pi}\int_0^\infty \int_0^\infty \frac{a\mathrm{Q} \cos \lambda x \cos \gamma\lambda}{\pi(\gamma^2+a^2)} \, d\lambda \, d\gamma. \qquad \text{(V.}a\text{)}$$

Thus we must identify the integrals in (V.a) and (V:), and this gives

$$\mathrm{A} = \frac{2a\mathrm{Q}}{\pi^2(\mathrm{E}+\mathrm{K}\lambda)}\int_0^\infty \frac{\cos \lambda\gamma \, d\gamma}{\gamma^2+a^2}.$$

Substituting for A in (IV.), we reach the solution

$$v = \frac{\mathrm{Q}}{4\pi\mathrm{K}} \log\left(\frac{x^2+\overline{y-a}^2}{x^2+\overline{y+a}^2}\right)$$

$$+ \frac{2a\mathrm{Q}}{\pi^2}\int_0^\infty \int_0^\infty \frac{e^{\lambda y} \cos \lambda x \cos \lambda\gamma}{(\mathrm{E}+\mathrm{K}\lambda)(\gamma^2+a^2)} \, d\lambda \, d\gamma.$$

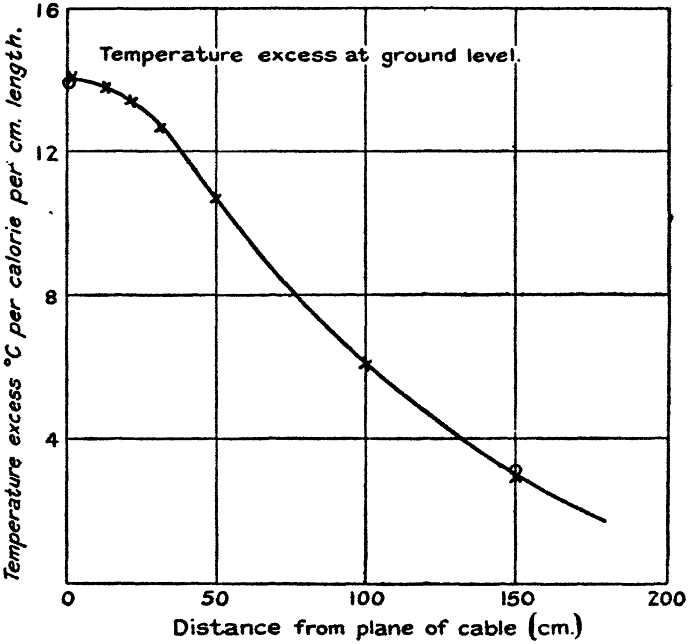
The integration with regard to γ, viz.,

$$\int_0^\infty \frac{\cos\lambda\gamma}{\gamma^2+a^2}\,d\gamma,$$

may be carried out. It reduces to $\frac{\pi e^{-a\lambda}}{2a}$, so that the *final expression* is

$$v=\frac{\mathrm{Q}}{4\pi\mathrm{K}}\log\left(\frac{x^2+\overline{y-a}^2}{x^2+\overline{y+a}^2}\right)+\frac{\mathrm{Q}}{\pi}\int_0^\infty \frac{e^{\lambda(y-a)}\cos\lambda x}{\mathrm{E}+\mathrm{K}\lambda}\,d\lambda.$$

Fig. 2.



I have not succeeded in reducing this integral further, but it may easily be evaluated numerically by plotting the integrand and measuring the area of the curve with a planimeter. Or it could possibly be expanded as a series in λ.

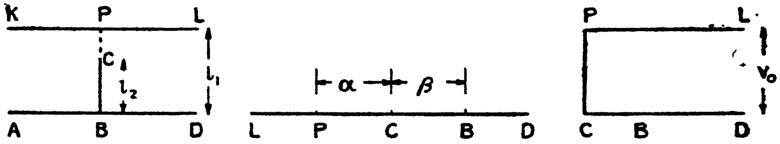
The temperatures on the ground, where $y=0$ and the first term vanishes, were calculated for the case $a=76$ cm. (*i. e.*, about 2 ft. 6 in.), $\mathrm{Q}=1$, $\mathrm{E}=0{\cdot}00025$, $\mathrm{K}=0{\cdot}0045$, and the results are shown in fig. 2. They were calculated by quadratures, using Simpson's rule with 11 ordinates, and checked at the first and last of the calculated points by using 27 ordinates.

Since the excess in temperature immediately over the cable is proportional to Q, its actual value may easily be deduced for a cable buried 2 ft. 6 in. in ground of about these thermal characteristics. For an ordinary 3-core cable of diameter 0·15 in. and carrying 150 amp., Q is approximately 1/30 calorie (per cm. run per sec.), so that the temperature excess will be 1/30 of that shown in the figure (for which Q=1).

4. *Example* II.—*Girder projecting into Insulation.*

We must solve first the corresponding problem with the boundary as an isothermal. In fig. 3 the left-hand portion shows a section perpendicular to the girder; DBA and CB are to be one isothermal, and KL another. It is obvious by symmetry that CP will be a line of heat flow. The diagram on the right of fig. 3 is the corresponding diagram, in the w plane, where $w=u+iv$, u being the flow function and v the temperature. To transform the one diagram into the other, we represent each conformally on the real axis in the "t" plane (centre portion of diagram, lettered similarly to the others).

Fig. 3.



The equations for the transformations are given by the Schwarz-Christoffel theorem * and take the forms

$$\frac{dz}{dt}=\mathrm{A}(t+\alpha)^{-\frac{1}{2}}(t-\beta)^{-\frac{1}{2}},$$

$$\frac{dw}{dt}=\mathrm{B}(t+\alpha)^{-\frac{1}{2}}t^{-\frac{1}{2}},$$

of which the solutions are

$$z=\mathrm{A}\cosh^{-1}\left(\frac{2t+\alpha-\beta}{\alpha+\beta}\right)+\mathrm{C}, \quad . \quad . \quad . \quad (\mathrm{I.})$$

$$w=\mathrm{B}\cosh^{-1}\left(\frac{2t+\alpha}{\alpha}\right)+\mathrm{D}. \quad . \quad . \quad . \quad . \quad (\mathrm{II.})$$

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* Forsyth, 'Theory of Functions,' 3rd edition, p. 665.

The constants of integration will be chosen so that $C=D=0$ and

$$A=l_1/\pi, \qquad B=v_0/\pi. \quad . \quad . \quad . \quad . \quad \text{(III.)}$$

This involves taking B as origin in the z plane, and C in the w plane. It introduces the known constants l_1 and v_0, the width of the strip, and the temperature difference across it, as marked in the diagram. The remaining quantity which is known *a priori*, viz., l_2, the depth of the girder, is related to α/β by the equation

$$\pi l_2=-il_1\cosh^{-1}(\alpha-\beta)/(\alpha+\beta).$$

Using (III.), the result of eliminating t between (I.) and (II.) is

$$\alpha\left(\cosh\frac{w\pi}{v_0}-1\right)=(\beta-\alpha)+(\beta+\alpha)\cosh\pi z/l_1. \quad \text{(IV.)}$$

Now, since $w=u+iv$, $z=x+iy$, the real and imaginary parts of this equation may be separated and equated independently. The result is

$$\alpha\left(\cosh\frac{u\pi}{v_0}\cos\frac{v\pi}{v_0}-1\right)=(\beta-\alpha)+(\beta+\alpha)\cosh\pi x/l_1\cos\pi y/l_1, \quad . \quad . \quad . \quad \text{(V.)}$$

$$\alpha\sinh\frac{u\pi}{v_0}\sin\frac{v\pi}{v_0}=(\beta+\alpha)\sinh\pi x/l_1\sin\pi y/l_1. \quad . \quad \text{(VI.)}$$

In the present problem, u may be eliminated at this stage by using the relation

$$\cosh^2\theta-\sinh^2\theta=1,$$

and this leads to the single equation

$$\begin{aligned}\cos^2\frac{\pi v}{v_0}\sin^2\frac{\pi v}{v_0}=\beta^2\sin^2\frac{\pi v}{v_0}&+(\alpha+\beta)^2\sin^2\frac{\pi v}{v_0}\cosh^2\frac{\pi x}{l_1}\cos^2\frac{\pi y}{l_1}\\&+2\beta(\alpha+\beta)\sin^2\frac{\pi v}{v_0}\cosh\frac{\pi x}{l_1}\cos\frac{\pi y}{l_1}\\&-(\alpha+\beta)^2\cos^2\frac{\pi v}{v_0}\sinh^2\frac{\pi x}{l_1}\sin^2\frac{\pi y}{l_1}. \quad . \quad . \quad \text{(VII.)}\end{aligned}$$

This is the (implicit) equation for v_1, referred to in paragraph 2. By its construction, v reduces to v_0 when $y=l_1$, *i. e.*, over the upper surface of the strip.

To solve the generalized problem, where Newton's law holds over the upper surface, we shall, following the procedure outlined in paragraph 1, add to v a quantity v_2 which is harmonic and vanishes over the lower boundary, but such that $(v+v_2)$ obeys Newton's law over the upper boundary.

To satisfy the first two conditions, we may take

$$v_2 = \mathrm{A}\int_0^{\infty} \sinh my \sin mx \, dm,$$

so that

$$\frac{\partial v_2}{\partial y} = \mathrm{A}\int_0^{\infty} m \cosh my \sin mx \, dm. \quad . \quad \text{(VIII.)}$$

Before imposing the third condition, we must evaluate $(\partial v/\partial y)_{y=l_1}$ from equation (VII.). On differentiating that equation, we obtain, after some reduction :

$$\begin{aligned}\frac{1}{v}\frac{\partial v}{\partial y}\sin\frac{\pi v}{v_0}\cos\frac{\pi v}{v_0} & \\ \Big[\alpha^2\cos^2\frac{\pi v}{v_0} - \alpha^2\sin^2\frac{\pi v}{v_0} & - (\alpha+\beta)^2\cosh^2\frac{\pi x}{l_1}\cos^2\frac{\pi y}{l_1} \\ & - \beta^2 - 2\beta(\alpha+\beta)\cosh\frac{\pi x}{l_1}\cos\frac{\pi y}{l_1} \\ & - (\alpha+\beta)^2\sinh^2\frac{\pi x}{l_1}\sin^2\frac{\pi y}{l_1}\Big] \\ = -\frac{1}{l_1}\sin\frac{\pi y}{l_1}\Big[\sin^2\frac{\pi v}{v_0} & \\ & \left\{(\alpha+\beta)^2\cosh^2\frac{\pi x}{l_1}\cos\frac{\pi y}{l_1} + \beta(\alpha+\beta)\cosh\frac{\pi x}{l_1}\right\} \\ & + \cos^2\frac{\pi v}{v_0}\left\{(\alpha+\beta)^2\sinh^2\frac{\pi x}{l_1}\cos\frac{\pi y}{l_1}\right\}\Big].\end{aligned}$$

We cannot obtain the value of $(\partial v/\partial y)_{y=l_1}$ immediately from this equation, since at $y=l_1$ the factors $\sin \pi v/v_0$ and $\sin \pi y/l_1$ on the two sides of the equation, vanish. The limit of their ratio may be evaluated in the form

$$\frac{d\,(\sin \pi y/l_1)}{d\,(\sin \pi v/v_0)} = \frac{v_0}{l_1}\Big/\left(\frac{\partial v}{\partial y}\right)_{y=l_1},$$

and then $\Big($setting $v=v_0$, $y=l_1$ with this value for the limit of $\dfrac{\sin \pi y/l_1}{\sin \pi v/v_0}\Big)$ we obtain $\left(\dfrac{\partial v}{\partial y}\right)_{y=l_1}$ in the form

$$\frac{v_0(\alpha+\beta)\sinh \pi x/l_1}{\sqrt{[\beta-(\alpha+\beta)\cosh \pi x/l_1]^2-\alpha^2}}. \quad . \quad . \quad \text{(IX.)}$$

(As a check to the algebra, the same value of the limit was obtained by determining it directly from the undifferentiated equation (VII.)). We are now in a position to satisfy the equation expressing Newton's law,

$$\mathrm{E}(v+v_2-v_0)=-\mathrm{K}\left(\frac{\partial v_1}{\partial y}+\frac{\partial v_2}{\partial y}\right)\quad \text{at } y=l_1,$$

where v_0 is now taken as the air temperature above the strip. Substituting the values of v, v_2 and their derivatives from (VII.), (VIII.), and (IX.), and writing $\mu(x)$ to represent $\sqrt{[\beta-(\alpha+\beta)\cosh \pi x/l_1]^2-\alpha^2}$, this becomes

$$\mathrm{EA}\int_0^\infty \sinh ml_1 \sin mx\, dm$$

$$=-\mathrm{K}\left[\frac{v_0(\alpha+\beta)\sinh \pi x/l_1}{\mu(x)}+\mathrm{A}\int_0^\infty m\cosh ml_1 \sin mx\, dm\right].$$

Rearranging this equation, it becomes

$$-\mathrm{A}\int_0^\infty \sin mx\,(\mathrm{E}\sinh ml_1+\mathrm{K}m\cosh ml_1)\,dm$$

$$=\frac{\mathrm{K}v_0(\alpha+\beta)\sinh \pi v/l_1}{\mu(x)},$$

and by Fourier's Theorem, the right-hand side is

$$\frac{2}{\pi}\int_0^\infty\int_0^\infty \frac{\mathrm{K}v_0(\alpha+\beta)\sinh \pi\lambda/l_1}{\mu(\lambda)}\,\frac{\sin m\lambda \sin mx}{}\,d\lambda\, dm.$$

Thus A must be taken as

$$-\frac{2}{\pi}\int_0^\infty \frac{\mathrm{K}v_0(\alpha+\beta)\sinh \pi\lambda/l_1 \sin m\lambda}{\mu(\lambda)[\mathrm{E}\sinh ml_1+\mathrm{K}m\cosh ml_1]}\,d\lambda,$$

and the *final result* is:

Temperature at $(x, y)=v+v_2$,

where v is given by equation (VII.) and

$$v_2=-\frac{2v_0\mathrm{K}(\alpha+\beta)}{\pi}$$

$$\int_0^\infty\int_0^\infty \frac{\sinh \pi\lambda/l_1 \sin m\lambda \sinh my \sin mx\, dm\, d\lambda}{[\mathrm{E}\sinh ml_1+\mathrm{K}m\cosh ml_1]\;\sqrt{[\beta-(\alpha+\beta)\cosh \pi\lambda/l_1]^2-\alpha^2}}.$$

It may be useful to collect here the meanings of the symbols occurring in this final result:—

v_0 = temperature of upper air, immediately over the strip;
l_1 = width of strip, so that upper surface is $y=l_1$;
E = heat loss per unit area per sec. per 1° excess above the air temperature;
K = thermal conductivity of the material in the strip.
α, β (which only occur in the form of their ratio) are connected with the depth of the girder (l_2) by the equation

$$\pi l_2 = -\imath l_1 \cosh^{-1}(\alpha-\beta)/(\alpha+\beta).$$

This final result is mathematically a complete solution to the problem which we set out to investigate, but since it is in the form of a double integral, it is not suitable for numerical application.

It is probably permissible to infer, since a comparatively simple problem leads to such a complex result, that the method given in this paper, although providing the general solution of the problem presented in the title, does not do so in a form suitable to the physicist. It is, however, the only discussion I have seen of the problem, and if in any physical application a result in *numerical* form is required, the resulting solution will have to be dealt with further in whatever manner is convenient, depending on the particular problem considered.

CXXX. *A Simple Proof and an Extension of Heaviside's Operational Calculus for Invariable Systems.* By BALTH. VAN DER POL, *D.Sc.* *.

§1. IN his book, 'Electromagnetic Theory,' which was published in the 'nineties of last century, Heaviside devised and made an extensive use of an operational method which enabled him to write down almost immediately the disturbance in any linear electrical (or mechanical) system resulting from the sudden application at the time $t=0$ of a given force. The system was supposed to be stable and, for $t<0$, to be in complete rest, *i. e.*, at first the coordinates with all their derivatives were supposed to be zero.

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* Communicated by the Author.

As a direct formal proof for the two important theorems deduced by Heaviside by means of his operational calculus was not given by him, some proofs were given at a later date by several writers.

The problem to which we will restrict ourselves in the present paper is that of the solution of a set of simultaneous linear differential equations with constant coefficients (representing therefore an invariable system) all the right-hand members of which are zero, except one, which represents the application of the given force. To begin with, we shall take for this force Heaviside's "unit function," which is defined as equal to zero for $t<0$ and unity for $t>0$.

Two solutions of practically the same nature, both leading up to the Heaviside symbolic solution of this problem, were published independently at practically the same date by Karl Willy Wagner* and by T. J. I'A. Bromwich†. Both authors analyse the "unit function," which we will denote by $[1]$, in the complex Fourier integral :

$$[1]=\frac{1}{2\pi i}\int_{c-\infty i}^{c+\infty i}\frac{e^{\nu t}}{\nu}d\nu. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Thereupon the response of the linear system to each of the frequencies ν could easily be obtained, and a final integration of all these responses to the individual frequencies of the continuous spectrum yielded the solution of the problem, the path of integration in the complex plane corresponding to the initial conditions of complete rest.

Bromwich's work is fully expounded in a book recently published by H. Jeffreys ‡.

Moreover, a proof was also given by J. R. Carson in 1917 §, who reduced the operational method to the solution of an integral equation. Carson and Heaviside himself applied the operational method to numerous problems connected with the propagation of disturbances over a cable, and a clear exposition of the whole matter based on his integral equation is to be found in Carson's book ‖. For further literature on this subject the reader may be referred to the books by Jeffreys and Carson. However, a very important contribution to our subject-matter, to which no reference is to be found yet in the books just mentioned, is contained in a little pamphlet of 20 pages by P. Lévy [*], who deduces the Heaviside operational calculus with the aid of Volterra's "*produit de composition*" of two functions, $f(t)$ and $g(t)$, which is written $f*g$ and defined as

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* *Arch. f. Electrotechnik*, iv. p. 159 (1916).

† Proc. London Math. Soc. xv. p. 401 (1916).

‡ H. Jeffreys, 'Operational Methods in Mathematical Physics' (Cambridge University Press, London, 1927).

§ Phys. Rev. x. p. 217 (1917).

‖ J. R. Carson, 'Electric Circuit Theory and the Operational Calculus' (McGraw-Hill Book Co., Inc., New York, 1926).

$$f*g=\int_0^t f(\tau)\,.\,g(t-\tau)d\tau. \quad . \quad . \quad . \quad (2)$$

In fact, Lévy points out that the solution of Carson's integral equation is given by the complex integral of Wagner and Bromwich, so that in Lévy's work the two originally divergent routes meet again [†].

It is the purpose of the present paper to give a very simple proof of the two operational solutions (first given by Heaviside and already referred to above) of the disturbance in an invariable linear system following upon the application of a "unit force" while the system was initially at rest. Our method enables us also easily to extend the solution to cases where the system originally is not at rest, and, moreover, where the force, which is suddenly applied at the time $t=0$, is not a constant but an arbitrary function of the time. In a later paper we hope to extend these considerations to equations with variable coefficients.

§ 2. Let us, in order to simplify the problem as much as possible, first consider the single differential equation

$$a_0\overset{(n)}{y}+a_1\overset{(n-1)}{y}+a_2\overset{(n-2)}{y}+\ldots\ldots+a_ny=[1], \quad . \quad . \quad (3)$$

where $\overset{(n)}{y}$ is written for $\dfrac{d^ny}{dt^n}$. Let, further, the initial conditions be given as

$$\text{for } t<0: \quad y=\overset{(1)}{y}=\overset{(2)}{y}=\ldots=\overset{(n-1)}{y}=0\,; \quad . \quad . \quad . \quad . \quad (4)$$

and let it further be assumed that the solutions are stable so that none of the roots have a positive real part. We observe that in this case, as in many others, it is much simpler to calculate $\int_0^\infty e^{-pt}y\,dt$ than y itself. For, in order to evaluate this integral, we multiply (3) by e^{-pt} and integrate between the limits zero and infinity. A typical term,

---

[*] Paul Lévy, 'Le Calcul symbolique d'Heaviside' (Gauthier-Villars, Paris, 1926). I am indebted to Dr. Le Corbeiller, of Paris, for drawing my attention to Lévy's work on the subject, which was also published in the *Bulletin des Sciences Mathématiques.*

[†] See also March, Bull. Am. Math. Soc. xxxiii. p. 311 (1927).

$$\int_0^\infty e^{-pt}\overset{(\rho)}{y}\,dt,$$

thus arising can easily be reduced by partial integrations by the aid of the initial conditions (4), for

$$\int_0^\infty e^{-pt}\overset{(\rho)}{y}dt=\left[e^{-pt}\overset{(\rho-1)}{y}\right]_0^\infty+p\int_0^\infty e^{-pt}\overset{(\rho-1)}{y}\,dt$$

$$=0+p\int_0^\infty e^{-pt}\overset{(\rho-1)}{y}\,dt.$$

By repeatedly integrating by parts we thus obtain

$$\int_0^\infty e^{-pt}\overset{(\rho)}{y}\,dt=p^\rho\int_0^\infty e^{-pt}y\,dt.$$

The right-hand member similarly becomes

$$\int_0^\infty [1]e^{-pt}\,dt=\int_0^\infty e^{-pt}\,dt=\frac{1}{p}.$$

Thus we obtain from (3):

$$\{a_0p^n+a_1p^{n-1}+a_2p^{n-2}+\ \ldots\ +a_n\}\int_0^\infty e^{-pt}y\,dt=\frac{1}{p}. \quad (5)$$

If we call the polynomial

$$a_0p^n+a_1p^{n-1}+a_2p^{n-2}+\ldots+a_n=\mathrm{H}(p),$$

we thus find immediately

$$\int_0^\infty e^{-pt}y\,dt=\frac{1}{p\mathrm{H}(p)}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is Carson's integral equation.

We notice that the polynomial $\mathrm{H}(p)$ of the left-hand member of (5) has exactly the same form as the left-hand member of our differential equation (3), except that $\frac{d^m}{dt^m}$ has been replaced by p^m. Thus the idea of operational solution arises, although p is nothing until now but an ordinary positive number.

So far, instead of having solved for y we have obtained an expression for $\int_0^\infty e^{-pt}y\,dt$ only. In all cases, however, where y can be expanded in a series of positive powers of t

the deduction of y from (6) is a simple matter; for let us assume y to be

$$y = b_0 + b_1 t + b_2 t^2 + b_3 t^3 + \ldots,$$

the integral of (6) then becomes

$$\int_0^\infty e^{-pt} y \, dt = \frac{1}{p}\left[b_0 + \frac{1\,!}{p} b_1 + \frac{2\,!}{p^2} b_2 + \frac{3\,!}{p^3} b_3 + \ldots\right]. \quad (7)$$

by virtue of the definition of the Gaussian Π-function:

$$\int_0^\infty e^{-pt} t^n \, dt = \frac{1}{p} \frac{\Pi(n}{p^n},$$

which, for integral positive values of n, becomes

$$= \frac{1}{p} . \frac{n\,!}{p^n}.$$

If, therefore, we expand the right-hand member of (6) in a series of negative powers of p:

$$\frac{1}{p\mathrm{H}(p)} = \frac{1}{p}\left(c_0 + \frac{c_1}{p} + \frac{c_2}{p^2} + \frac{c_3}{p^3} + \ldots\right), \quad . \quad . \quad (8)$$

and identify the corresponding terms of (7) and (8), we obtain:

$$b_0 = c_0,$$

$$c_1 = \frac{c_1}{1\,!},$$

$$b_2 = \frac{c_2}{2\,!},$$

$$b_3 = \frac{c_3}{3\,!},$$

$$\vdots$$

$$b_m = \frac{c_m}{m\,!}.$$

We thus find :—

Heaviside's power series expansion or *Operational Theorem No. 1:*

Write in the differential equation p^m *instead of* $\frac{d^m}{dt^m}$. *Thus obtain* H(p). *Expand* $1/\mathrm{H}(p)$ *in powers of* p^{-1}:

$$\frac{1}{\mathrm{H}(p)} = c_0 + \frac{c_1}{p} + \frac{c_2}{p^2} + \ldots;$$

write further $t^m/m!$ *instead of* p^{-m}, *and the resulting expression*

$$y=c_0+c_1\frac{t}{1!}+c_2\frac{t^2}{2!}+c_3\frac{t^3}{3!}+\ldots$$

is the solution of the differential equation for a "unit" applied force with the initial condition of complete rest.

We may write this result symbolically

$$y=\frac{1}{H(p)}. \quad \ldots \ldots \quad (9)$$

Moreover, Heaviside also gave another solution, leading up to Expansion theorem No. 2. Starting again from (6),

$$\int_0^\infty e^{-pt}y\,dt=\frac{1}{pH(p)}, \quad \ldots \ldots \quad (6)$$

we expect, from the nature of the problem, that y can also be written as follows:

$$y=C_0+C_1e^{p_1t}+C_2e^{p_2t}+\ldots+C_ne^{p_nt}, \quad \ldots \quad (10)$$

where the p's are the roots of $H(p)=0$.

Substituting (10) in (6), we get

$$\int_0^\infty e^{-pt}y\,dt=\frac{C_0}{p}+\frac{C_1}{p-p_1}+\frac{C_2}{p-p_2}+\frac{C_3}{p-p_3}+\ldots\frac{C_n}{p-p^n} \quad \ldots \ldots \quad (11)$$

On the other hand, the development of $\frac{1}{pH(p)}$ in partial fractions is well known to yield

$$\frac{1}{pH(p)}=\frac{1}{pH(0)}+\frac{1}{(p-p_1)p_1H'(p_1)}+\frac{1}{(p-p_2)p_2H'(p_2)}+\ldots$$
$$\ldots+\frac{1}{(p-p_n)p_nH'(p_n)}, \quad \ldots \quad (12)$$

where

$$H'(p_m)=\left(\frac{dH}{dp}\right)_{p=p_m}.$$

Identifying again corresponding terms in (11) and (12), we find

$$C_0=\frac{1}{H(0)},\quad C_1=\frac{1}{p_1H'(p_1)},\quad \ldots,\quad C_n=\frac{1}{p_nH'(p_n)};$$

and thus we find :—

Heaviside's second expansion or *Operational Theorem No.* 2 :

$$y=\frac{1}{\mathrm{H}(0)}+\frac{e^{p_1t}}{p_1\mathrm{H}'(p_1)}+\frac{e^{p_2t}}{p_2\mathrm{H}'(p_2)}+\ldots+\frac{e^{p_nt}}{p_n\mathrm{H}'(p_n)}, \quad (13)$$

where $p_1, p_2 \ldots, p_n$ *are the roots of* $\mathrm{H}(p)=0$.

It was supposed that all the roots p were different. As the extension to multiple roots does not yield any essentially new point, this case will not be discussed here.

§ 3. The method expounded above for finding $\int_0^\infty e^{-pt}y\,dt$ can now easily be extended to the case where the initial conditions are not of the form (4), but are given as

$$\text{for } t<0: \quad \left.\begin{array}{l} y = y\,(0) \\ \overset{(1)}{y} = \overset{(1)}{y}\,(0) \\ \overset{(2)}{y} = \overset{(2)}{y}\,(0) \\ \cdot \quad \cdot \quad \cdot \quad \cdot \\ \overset{(n-1)}{y} = \overset{(n-1)}{y}\,(0) \end{array}\right\}, \quad \ldots\ldots \quad (14)$$

where

$$\overset{(m)}{y}\,(0)=\left(\frac{d^my}{dt^m}\right)_{t=0}.$$

Again we assume the "unit" force to be applied at the instant $t=0$.

Proceeding in the same way as before, we multiply (3) throughout by e^{-pt} and integrate between zero and infinity. The partial integrations now make instant use of the initial conditions, and we find

$$\begin{aligned} p\mathrm{H}(p)\int_0^\infty e^{-pt}y\,dt \\ =1+a_0[p\,\overset{(n-1)}{y}\,(0)+p^2\,\overset{(n-2)}{y}\,(0)+p^3\,\overset{(n-3)}{y}\,(0)+\ldots+p^n\ y(0)] \\ +a_1[p\,\overset{(n-2)}{y}\,(0)+p^2\,\overset{(n-3)}{y}\,(0)+\ldots+p^{n-1}y(0)] \\ +a_2[p\,\overset{(n-4)}{y}\,(0)+\ldots+p^{n-2}y(0)] \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\ +a^{n-1}py\,(0)\,; \end{aligned}$$

or, after grouping together the terms relating to each initial condition,

$$
\begin{aligned}
\mathrm{H}(p)\int_0^\infty e^{-pt}y\,dt
&=\frac{1}{p}+y(0)\left[a_0p^{n-1}+a_1p^{n-2}+a_2p^{n-3}+\,\ldots\,+a_{n-1}\right]\\
&\qquad+\overset{(1)}{y}(0)\left[a_0p^{n-2}+a_1p^{n-3}+\,\ldots\,+a_{n-2}\right]\\
&\qquad\qquad+\overset{(2)}{y}(0)\left[a_0p^{n-3}+\,\ldots\,+a_{n-3}\right]\\
&\qquad\qquad\qquad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\
&\qquad\qquad\qquad\qquad+\overset{(n-1)}{y}(0)\,a_0,
\end{aligned}
$$

which expression can be written as

$$
\begin{aligned}
\mathrm{H}(p)\int_0^\infty e^{-pt}y\,dt=\frac{1}{p}+y(0)\left[\frac{\mathrm{H}(p)}{p}\right]+\overset{(1)}{y}(0)\left[\frac{\mathrm{H}(p)}{p^2}\right]&\\
+\overset{(2)}{y}(0)\left[\frac{\mathrm{H}(p)}{p^3}\right]+\,\ldots\,\overset{(n-1)}{y}(0)\left[\frac{\mathrm{H}(p)}{p^n}\right]&, \qquad . \;\; . \;\; .(15)
\end{aligned}
$$

where by $\left[\frac{\mathrm{H}(p)}{p^m}\right]$ is meant *that* part only of $\frac{\mathrm{H}(p)}{p^m}$ which contains positive powers of p, the zero'th power included, the rest being omitted.

In the same symbolic way in which (9) was expressed we now obtain from (15)

$$
\begin{aligned}
\frac{y}{p}=\frac{1}{p\mathrm{H}(p)}+y(0)\frac{1}{\mathrm{H}(p)}\left[\frac{\mathrm{H}(p)}{p}\right]&\\
+\overset{(1)}{y}(0)\frac{1}{\mathrm{H}(p)}\left[\frac{\mathrm{H}(p)}{p^2}\right]+\,\ldots\,+\overset{(n-1)}{y}(0)\frac{1}{\mathrm{H}(p)}\left[\frac{\mathrm{H}(p)}{p^m}\right]&. \qquad . \;\; . \;\; . \;\; (16)
\end{aligned}
$$

When, in the same way as in the former problem, this expression (16) is written as a power series in p^{-1}, and thereupon the symbolic solution thus obtained is "algebrized" (which is Heaviside's expression, meaning the replacement of p^{-m} by $t^m/m\,!$), we obtain the solution of our problem.

The form of (16) clearly shows the individual effects of each of the initial conditions. With

$$
y(0)=\overset{(1)}{y}(0)=\overset{(2)}{y}(0)=\,\ldots\ldots\,=\overset{(n-1)}{y}(0)=0,
$$

(16) is reduced to (9). Moreover, omitting the first t of the right-hand member (which was due to the impress "unit" force), we find a symbolic solution of (3) for th free oscillations resulting from the initial conditions (14) only, there being no external force. That (16) is the sum of these two solutions is a consequence of the linearity of the problem.

§ 4. An extension to the operational treatment of a system of simultaneous differential equations will be obvious.

Let it be given by:

$$\left.\begin{array}{l} \alpha_{11}(D)y_1+\alpha_{12}(D)y_2+\ \dots\ +\alpha_{1n}(D)y_n=0 \\ \alpha_{21}(D)y_1+\alpha_{22}(D)y_2+\ \dots\ +\alpha_{2n}(D)y_n=0 \\ \dots\dots\dots\dots\dots \\ \alpha_{n1}(D)y_1+a_{n2}(D)y_2+\ \dots\ +\alpha_{nn}(D)y_n=[f(t)] \end{array}\right\} \quad 17)$$

where $\alpha_{rs}(D)=a_{rs}D^2+b_{rs}D+c_{rs}=a_{rs}\dfrac{d^2}{dt^2}+b_{rs}\dfrac{d}{dt}+c_{rs}$.

The set of equations (17) is relevant to an electrical or mechanical system at a certain point of which a force $f(t)$ is applied at the time $t=0$, which we indicate by the brackets: $[f(t)]$.

Again we multiply each of the equations with e^{-pt} and integrate between zero and infinity. As in our first problem, the integrals can be integrated by parts, yielding a specially simple result as a consequence of the initial conditions:

$$y_1(0)=\overset{(1)}{y}_1(0)=y_2(0)=\overset{(1)}{y}_2(0)=\dots=y_n(0)=\overset{(1)}{y}_n(0)=0.$$

We thus obtain

$$\left.\begin{array}{l} \alpha_{11}(p)Y_1+\alpha_{12}(p)Y_2+\ \dots\ +\alpha_{1n}(p)Y_n=0, \\ \alpha_{12}(p)Y_1+\alpha_{22}(p)Y_2+\ \dots\ +\alpha_{2n}(p)Y_n=0, \\ \dots\dots\dots\dots\dots \\ \alpha_{n1}(p)Y_1+\alpha_{n2}(p)Y_2+\ \dots\ +\alpha_{nn}(p)Y_n=\displaystyle\int_0^\infty e^{-pt}[f(t)]dt, \end{array}\right\} \quad \dots \quad (18)$$

where
$$Y_1=\int_0^\infty e^{-pt}y_1dt,$$
$$Y_2=\int_0^\infty e^{-pt}y_2dt,$$
$$\dots\dots\dots$$
$$Y_n=\int_0^\infty e^{-pt}y_ndt.$$

Further, it will be obvious that

$$\int_0^\infty e^{-pt}[f(t)]\,dt = \int_0^\infty e^{-pt}f(t)\,dt,$$

as was the case with the "unity" function of the first problem.

The solution of any one of the Y's in (14) is

$$\mathrm{Y}_r = \frac{\Delta_r}{\Delta}\int_0^\infty e^{-pt}f(t)\,dt, \quad . \quad . \quad . \quad . \quad (19)$$

where Δ is the complete determinant of the system, and Δ_r its minor with respect to the *r*th term in the last row. Dropping the suffix *r*, we write this result

$$\mathrm{Y} = \int_0^\infty e^{-pt}y(t)\,dt = \frac{\mathrm{F}(p)}{\Delta(p)}\int_0 e^{-pt}f(t)dt, \quad . \quad (20)$$

so that the integral equation (of Laplace type) for the unknown $y(t)$ is

$$\int_0^\infty e^{-pt}\left\{y(t) - \frac{\mathrm{F}(p)}{\Delta(p)}f(t)\right\}dt = 0, \quad . \quad . \quad (21)$$

where $f(t)$ is the force applied at the instant $t=0$, and where, from the nature of the problem, in which a stable system is assumed, the denominator has no roots with positive real parts, so that the Hurwitz conditions for $\Delta(p)$ are fulfilled. (20) or (21) are of the same form as (6), so that the two operational solutions given before can here again be applied to solve for y either as a series expansion in t or as a sum of characteristic vibrations. Moreover, if the initial values of the various differential coefficients are different from zero, it is possible to express the solution of the system in the same way as we did for a single equation. Thus the general problem of the behaviour of an invariable system, starting from any given initial conditions and acted upon by a force given as a function of the time, is found to be solvable by the aid of the above extension of Heaviside's operational calculus.

Natuurkundig Laboratorium der
N. V. Philips's Gloeilampenfabrieken,
Eindhoven, January 1929.

CXXXI. *Certain Molecular Lengths measured by an Optical Lever.* *By* W. N. Bond, *M.A., D.Sc., F.Inst.P., Lecturer in Physics in the University of Reading* *.

Contents.

Summary.
Preliminary Experiments.
Apparatus used.
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Summary.

The development, construction, and use of optical levers is described that enable certain single changes in the thickness of a sheet of mica to be measured to an accuracy of about $1 \cdot 5 \times 10^{-8}$ cm. On tilting the lever and letting it return gently on to the mica, apparent changes in thickness are observed. These changes are analysed for periodicity. The periodicity found with muscovite mica,

$$(10 \cdot 0 \pm 0 \cdot 3) . 10^{-8} \text{ cm.},$$

is concluded to correspond to the length of the unit cell of muscovite, $9 \cdot 95 \times 10^{-8}$ cm. (as deduced from X-ray experiments). Steel, similarly, yielded a periodicity of

$$(6 \cdot 8 \pm 0 \cdot 2) . 10^{-8} \text{ cm.},$$

which is attributed to the length of the cementite unit cell, $6 \cdot 737 \times 10^{-8}$ cm. (according to X-ray measurements).

It is shown that, in *each* of the four experiments described, so marked a periodicity so close to a possible X-ray value would only occur spuriously once in about 100 such experiments.

The results seem best explained by assuming that the needle-tip of the lever ruptures a certain number of the surface-layers of the crystal, these layers flowing radially outwards till the needle reposes on the first intact layer. If flow did not occur, it is estimated that pressures of from 30,000 to 180,000 atmospheres would have occurred at the contact. It is found necessary to conclude that a more or less ordered return flow of a small number of the surface-layers occurs when the needle-tip is withdrawn. This return flow is

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* Communicated by the Author.

attributed to surface-tension or cohesion forces. Some experiments using selenite gave no evidence of any corresponding periodicity. This may have been due to the plastic nature of selenite, or to some experimental error.

Preliminary Experiments.

ABOUT three years ago an optical lever was constructed having an effective length of 1·3 mm., the legs consisting of three small ball-bearings soldered into the base of a piece of brass The two outer legs rested in a slot and hole in the flat top of a brass block, the central leg resting on a flat on the block (or, later, on a ball-bearing fastened in the block). To facilitate a lever of such a small effective length remaining in stable equilibrium, a thin rubber band was arranged to pull the lever on to its support, the resultant force passing through the very flat isosceles triangle formed by straight lines joining the tips of the three legs.

This lever, when used with a lamp and scale at a metre distance, easily gave readings of the thickness of sheets of mica, or repeated zero settings, to an accuracy of 10^{-5} cm. As only quite rough usage moved the zero by more than that amount, it was decided to try to improve on the apparatus. The possibility was at that time considered of measuring the effective length of a mica molecular or unit cell by determining the thickness of a mica sheet at various points.

The designs of various types of measuring machine were considered, and considerable time was spent in attempting to form double levers of various forms that had geometrical constraints. These levers were, however, not very successful.

It seemed possible to improve the sensitivity of a single optical lever by obtaining a setting accurate to within a fraction of the width of the central diffraction band in the image of an illuminated slit. Early in 1928 I found a paper by Dr. C. V. Burton * showing that it was possible to take readings to very considerably less than the half-width of the central diffraction band, and work on these lines was commenced. The use of optical interference was thought inadvisable, as it does not easily lend itself to the measurement of other than gradual movements, and might necessitate the use of a heavy lever. For reasons of complication Prof. Whiddington's ultra-micrometer was also avoided. The single optical lever has the advantage that all the measurements required are three lengths.

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* Phil. Mag., March 1912, p. 385.

In the first of these experiments the lever of effective length 1·3 mm. was used. The return beam of light formed an image of a fine illuminated slit at a point effectively 50 cm. from the mirror, and this image was viewed with a Hilger travelling microscope (reading to 1/100 mm. and to 1/1000 mm. by estimation). Following Dr. Burton's method, accurate setting was obtained by almost eclipsing the central diffraction band in the image by a wire in the eyepieee of the microscope. In every case several settings of the microscope were made in succession between successive tiltings of the lever. The results showed considerable accuracy. For instance, without using any mica the lever was tilted and allowed to return to zero five times, and between these tiltings sets of microscope settings were made. Averaging each group of microscope settings, it was found that successive mean readings did not differ by more than about 10^{-7} cm.

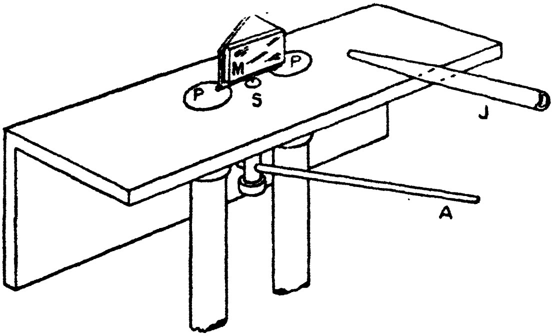
A flake of mica was then placed between the central leg of the lever and the fixed steel ball on which it had previously rested. On tilting the lever and letting it return, larger changes in reading were obtained than when the mica was not present, and these were at that time attributed to lateral shifting of the mica having occurred when the lever was tilted. The observational error was, however, still rather too large to tell whether the changes between one reading and the next did or did not correspond to small integral multiples of the length of the mica unit cell.

Apparatus used.

Since the results with the improved optical arrangement had been nearly accurate enough to give definite evidence for or against the possibility of detecting the molecular spacing by this means, it was decided to attempt to obtain about a ten-fold increase in sensitivity. As 1/1000 mm. seemed as small as it was convenient to measure accurately at the last stage of the system, it was decided not to follow Dr. Burton's method of actuating the micrometer screw by another screw, but to increase the optical path three-fold and decrease the length of the lever to a third or less. (The latter, if it were possible, would also decrease the relative effect of external disturbances.) To overcome the difficulty of obtaining stability of such a short lever, it was decided to use a steel lever the outer legs of which rested on the poles of a horse-shoe magnet. The centre of gravity of the lever could then be at any reasonable distance from the vertical plane through the outer legs, provided it were on the same side of this plane as the central leg.

The optical lever.—Each lever used consisted of a short length of "hack-saw" blade L (fig. 1) about 1 cm. by 1 cm., at each end of the lower edge of which a 1/32 inch diameter steel ball-bearing was soldered. At the centre of the lower edge either a third ball-bearing or the tip of a fine needle was soldered, not quite in line with the outer ball-bearings. (The imaginary plane touching the lower surface of the three legs must be as nearly perpendicular to the plane of the lever itself as possible.) To one face of the steel blade a thin mirror M (4 mm. by 9 mm.) was fastened with soft wax.

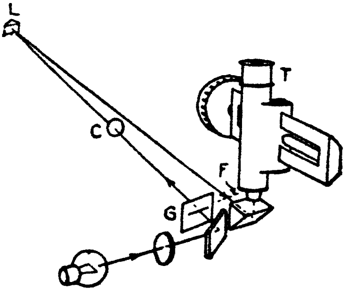
Fig. 1.



The support for the lever.—Two cobalt-steel 3/8-inch diameter bar magnets were fitted at the top with steel pole-caps PP (fig. 1) and joined by an iron yoke at the bottom. The steel pole-caps were soldered into holes in one face of a stout brass "angle-piece," and half-way between the pole-caps the end of a hardened steel screw S came approximately flush with the top of the brass plate. The brass and pole-caps were polished flush and reasonably plane, and the tip of the central steel screw was made slightly convex so that any thin mica sheet pressed into contact with it by the central leg of the lever would not be constrained by the screw tip except close to the one point of contact. The central screw could be turned by means of a "tommy-bar" A to adjust the optical lever till the plane of the mirror was vertical. The magnetic attraction between the outer legs of the lever and the magnet pole-caps on which they rest prevents sliding of the lever, even when the lever is intentionally tilted (unless the tilting is roughly performed). A hole-and-slot constraint in the pole-caps was not used, as it would increase the friction unduly.

The general arrangement of the apparatus.—The arrangement of the apparatus is illustrated in fig. 2. Light from one filament of an 8-volt "galvanometer lamp," passed through the convex lens in the lamp-fitting, was reflected from a mirror and passed through a fine slit G produced by ruling with a needle a fine line through the silvering of a glass mirror. The light then passed through an achromatic convex lens C (of about 33 cm. focal length) to the optical lever L. The return beam of light passed just to one side of C and produced an image of the slit G at a point F. The light was then reflected by a right-angled prism and passed into the travelling microscope T, which was adjusted to view the image at F. (After preliminary adjustment, all the apparatus was kept fixed with the exception of the lever L and the microscope T.)

Fig. 2.



It was found convenient and satisfactory not to obtain accurate setting of the microscope by eclipsing the central diffraction band by a wire in the microscope eyepiece, but by setting a spider thread in the eyepiece centrally along the band.

Apparatus to tilt the lever.—In the present experiments the tilting of the lever was performed from a distance. In most cases a rubber bulb held in the hand was used to produce a small blast of air through the jet J (fig. 1) which tilted the lever by an amount that could be fairly controlled. In a few cases a copper wire moved by an electromagnetic relay was used to produce the tilting.

Experimental Results.

In the first experiments performed with this apparatus (a brief account of which was given in a letter to 'Nature'*), the tilting of the lever was performed by means of the tip of a pencil held in the hand. Dummy experiments showed that a correction for a general drift of the readings was necessary. This trouble was largely overcome in the subsequent experiments by tilting the lever without approaching it, as described in the previous section of this paper. This, and the increased rapidity with which the experiments could be performed, reduced any error due to drift. No drift or other correction was applied to any of the measurements given in the present paper.

The central leg of the lever could be arranged to rest on the tip of the steel screw S (fig. 1), or a loose flake of mica could be interposed, or the mica could be cemented down to the screw S with sealing-wax. In each set of experiments the lever was tilted so that its central leg no longer rested on S, and then the lever was allowed to descend again gently. A series of ten microscope settings on the image F (fig. 2) was then carried out, and the lever again tilted and the process repeated. The mean of each group of microscope settings was then calculated. These means may conveniently be designated "microscope readings." Consecutive microscope readings were then subtracted. This process of subtraction largely eliminates error due to a temporary or exponential drift that occurred just after descent of the lever.

These changes in the microscope reading, resulting from the tilting of the lever, were at first attributed to a lateral shifting of the mica (that was resting freely on the top of the screw S). It was however found that similar changes occurred even when the mica was cemented to S; and similar, though generally smaller, changes occurred when the leg of the lever rested directly on the screw S, without any mica between. The probable cause of these changes in microscope reading and the analysis of the changes for periodicity are considered later in the paper. It may be noted, however, that all the specially large changes were in the sense corresponding to a decrease in the thickness of the mica, but that the smaller changes corresponded more usually to an increase in the mica thickness.

In the present experiments the central leg of the levers consisted of the tip of a "No. 10" needle (in place of the

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* 'Nature,' Aug. 4th, 1928, p. 169.

1/32-inch diameter steel ball previously used*). The effective length of the levers was measured directly by means of a travelling microscope. The details of the levers are given below:—

TABLE I.

Details of Optical Levers used.

Lever.	Nature of tip of central leg.	Radius of curvature of tip of leg.	Effective length of lever (cm.).	Mass of lever.
a	"No. 10" needle	—	0·0115 ±0·0005	0·42 gm.
b	The same re-sharpened	$0{\cdot}001_0$ cm.	0·0120 ±0·0003	

The general properties of the mica used in these experiments are recorded in the following table:—

TABLE II.

Properties of the Mica used.

White and biaxal. Value of 2E compared with that for a specimen of muscovite:—

Present sample.............. 26½ } scale-divisions.
Specimen of muscovite...... 26½ }

The principal refractive indices of the present specimen, for sodium light, were found:—

$$\alpha = 1{\cdot}563_1$$
$$\beta = 1{\cdot}593_6$$
$$\gamma = 1{\cdot}598_9.$$

(These fall within the range given by muscovite.)

The measurements obtained in the lever experiments, using a flake of mica, are recorded in Tables III. and IV. The results of experiments in which no mica was used, the needle-tip of the lever resting directly on the steel screw S (fig. 1), are given in Tables V. and VI. The analysis of these results for periodicity and the meaning of the results are considered in the following sections of the paper.

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* 'Nature,' *loc. cit.*

TABLE III.

Mica experiments (mica resting freely on screw S, fig. 1).
Lever length : 0·011,5±0·000,5 cm.
Distance LF (fig. 2) : 161·8±0·1 cm.

Differences between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.

(+ corresponds to an increased *descent* of the lever.

+ 1·2
+ 94·0
− 80·0
+ 3·5
+ 7·9
−164·3
+143·6
+ 25·7
+ 54·0

+ 60·5
+ 30·6
− 0·3
− 3·9
+184·1
− 2·3
+ 35·6
+ 28·2
+ 36·4
+169·9
− 94·7
+ 81·8

TABLE IV.

Mica experiments (mica cemented to screw S, fig. 1).
Lever length : 0·012,0±0·000,3 cm.
Distance LF (fig. 2) : 114·9±0·1 cm.

Differences between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.

(+ corresponds to an increased *descent* of the lever.)

− 72·8
− 4·4
+474·2
−110·2
− 22·6
+476·2
−166 3
− 0·7
+219·3
−155·9
+279·5

− 32·0
− 1·5
− 129·8
− 112·4
+ 23·0
+1006·9
− 109·0
− 48·6

TABLE V.

Steel experiments.
Lever length : 0·011,5 ± 0·000,5 cm.
Distance LF (fig. 2) : 115·5 ± 0·1 cm.

Difference between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.

(+ corresponds to an increased *descent* of the lever.)

− 7·6	+10·0
−10·3	+14·9
−21·7	−37·1
−27·8	−13·4
−11·2	−28·4
−60·8	+25·4
− 0·2	−14·6
−28·3	−12·6
−23·3	+52·8

TABLE VI.

Steel experiments.
Lever length : 0·012,0 ± 0·000,3 cm.
Distance LF (fig. 2) : 115·2 ± 0·1 cm.

Difference between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.

(+ corresponds to an increased *descent* of the lever.)

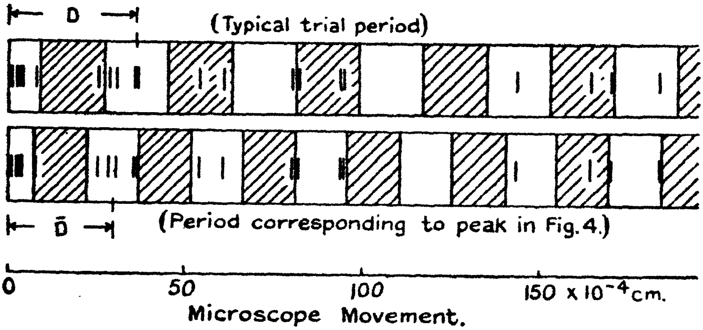
−15·9	− 25·2
+ 1·8	−214·2
−24·1	+119·9
−23·7	− 18·9
+ 25·9	+204·8
−14·6	− 26·0
−34·7	+ 0·7
−15·1	+607·5
+17·9	− 15·7
−29·4	± 0·0
−12·7	

Analysis of the Results for Periodicity.

If the differences between consecutive microscope readings contained any periodicity due to the mica (or steel) consisting of an array of unit or molecular cells such as is revealed by X-ray analysis, the periodicity would probably not be of sine form, but would consist of a series of isolated peaks separated by distances that are various integral multiples of some presumed "unit length." Experimental errors would have the effect of broadening the peaks, and for their detection it is necessary that the average experimental error shall be appreciably less than an amount corresponding to half the "unit length."

The most suitable test for such a periodicity, which gives equal "weight" to each observation, and which does not involve excessive calculation, consists in assuming in turn various trial values D for the "unit length" and finding what number of observations fall nearer to integral multiples of the "unit length" than to the intermediate odd multiples of the half "unit length" (indicated in fig. 3 by their falling in the unshaded rather than the shaded spaces). The result of such an analysis of the measurements recorded in Table III. is shown graphically in fig. 4 *.

Fig. 3.



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* The peak may be made to appear considerably more prominent by plotting as ordinates not the number of observations falling in the "unshaded" parts, but, for instance, the *ratio* of this number of observations to the number falling in the "shaded" parts (see Phil. Mag. 1. p. 640, 1925).

A well-defined peak is observed in the curve (fig. 4) with apex at $\overline{D}=29\cdot45\times10^{-4}$ cm. (at microscope), corresponding to about 10×10^{-8} cm. at the mica. (The best estimate of the value does not usually coincide exactly with the apex of the curve.) This periodicity is concluded to represent one due to the mica varying in thickness in some way by whole numbers of mica unit cells. The evidence for this peak not being a fortuitous one is given in the following section of the paper.

In fig. 3 the 21 changes in microscope reading given in Table III. are shown to scale, all being termed positive for convenience. The length $\overline{D}$ corresponds to the trial "unit length" that fits the results most successfully. For that trial "unit length" 18 of the 21 observations differ from integral multiples of the value of D by less than $\pm\frac{D}{4}$. The probability of any one at all of the 21 being more than $\frac{D}{2}$ in error is thus certainly less than 0·2. We may assume, therefore, that each observation corresponds to the integral multiple of $\overline{D}$ nearest to it. We may also assume that the changes of reading corresponding to a movement of zero molecular or unit cells should be zero, and hence neglect the 6 readings close to zero. Collecting in tabular form, we get:

Fig. 4.

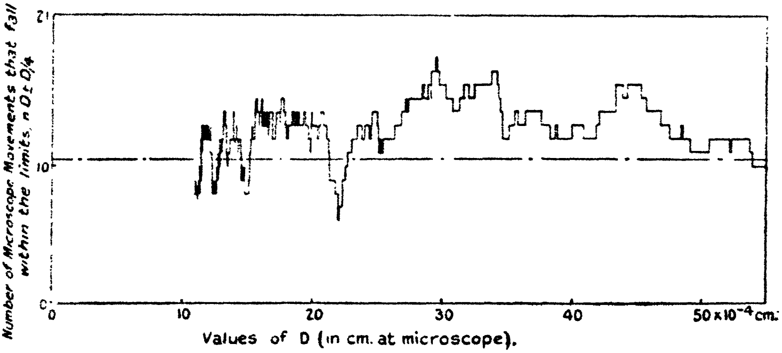

TABLE VII.

Changes in mica thickness. (From Table III.)

Number of molecular or unit cells increase.	Microscope change (in 10^{-4} cm.).	Deduced best estimate.	Residuals v.
+6	164·3	175·0	−10·7
+3	94·7 80·0	87·5	+ 7·2 − 7·5
0	3·9 2·3 0·3 1·2 3·5 7·9	0	+ 3·9 + 2·3 + 0·3 − 1·2 − 3·5 − 7·9
−1	25·7 28·2 30·6 35·6 36·4	29·2	+ 3·5 + 1·0 − 1·4 − 6·4 − 7·2
−2	54·0 60·5	58·3	+ 4·3 − 2·2
−3	81·8 94·0	87·5	+ 5·7 − 6·5
−5	143·6	145·8	+ 2·2
−6	169·9 184·1	175·0	+ 5·1 − 9·1
	Sum. = 1283·4 1283·4/44 = 29·17		$\Sigma \mid v \mid = 99{\cdot}1$

Hence :—

Probable error value of the deviation of a single change in microscope reading from the best estimate

$$= \pm 0{\cdot}845 \frac{99{\cdot}1}{\sqrt{21{\cdot}20}} \times 10^{-4} \text{ cm.} = \pm 4{\cdot}1 \times 10^{-4} \text{ cm.}$$

Mean value of microscope change for the length of one unit cell of mica

$$= \frac{1283{\cdot}4 \pm 4{\cdot}1 \sqrt{15}}{44} \times 10^{-4} \text{ cm.} = (29{\cdot}1_7 \pm 0{\cdot}36) \times 10^{-4} \text{ cm.}$$

Estimated length of unit cell of mica (see Table III.)

$$=\frac{(29{\cdot}1_7\pm0{\cdot}36)\,.\,10^{-4}\text{ cm.}\times(0{\cdot}001{,}5\pm0{\cdot}000{,}5)\text{ cm.}}{2\times(161{\cdot}8\pm0{\cdot}1)\text{ cm.}}$$

$$=(10{\cdot}3_5\pm0{\cdot}5)\times10^{-8}\text{ cm.}$$

Very similar calculations were made with the measurements contained in Tables IV., V., and VI. The four sets of results are collected in Table VIII. (Some measurements made using selenite did not give any evidence of a corresponding periodicity. This may have been due to the plastic nature of selenite or to some experimental error.)

TABLE VIII.

Nature of contact.	Lever length. (cm.)	Distance from lever to microscope (LF fig. 2). (cm.)	Peak of curve.		Deduced estimate of unit cell length.		
			Height.	Microscope movement. (cm.)	Microscope movement. (cm.)	Cell length. (cm.)	Mean. (cm.)
				$10^{-4}\times$	$10^{-4}\times$	$10^{-8}\times$	$10^{-8}\times$
Steel-mica	0·011,5 ±0·000,5	161·8 ± 0·1	18 in 21	$29{\cdot}4_5$	$29{\cdot}1_7$ ± 0·4	$10{\cdot}3_5$ ± 0·5	10·0 ± 0·3
	0·012,0 ±0·000,3	114·9 ± 0·1	16 in 19	18·9	18·8 ± 0·1	9·8 ± 0·3	
Steel-steel	0·011,5 ±0·000,5	115·5 ± 0·1	16 in 18	12·7	12·8 ± 0·2	6·4 ± 0·3	6·8 ± 0·2
	0·012,0 ±0·000,3	115·2 ± 0·1	18 in 21	13·5	13·5 ± 0·1	7·0 ± 0·2	

In the case of the muscovite mica the periodicity found in a direction perpendicular to the cleavage

$$(10{\cdot}0\pm0{\cdot}3)\,.\,10^{-8}\text{ cm.},$$

clearly corresponds to the distance between cleavage planes as obtained by X-ray analysis *,

$$9{\cdot}95\times10^{-8}\text{ cm.}$$

The two estimates of the periodicity given in Table VIII. differ from this value by less than their probable errors.

The experiments with steel give a periodicity of

$$(6{\cdot}8\pm0{\cdot}2)\,.\,10^{-8}\text{ cm.},$$

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* C. Mauguin, *Comptes Rendus*, p. 288, July 25th, 1927.

and this would be presumed to correspond to some unit cell length, or distance between cleavage planes. Three types of crystal have been found by X-ray methods, any of which might be concerned. These are :—

α, β, and δ ferrite * (body-centred cubic), sides of unit cell

$$2{\cdot}87 \,.\, 10^{-8} \text{ cm.},$$

γ ferrite † (face-centred cubic), sides of unit cell

$$\left.\begin{array}{r} 3{\cdot}601 \\ \text{to}\quad 3{\cdot}629 \end{array}\right\} 10^{-8} \text{ cm.},$$

cementite ‡ (Fe_3C) (orthorhombic), sides of unit cell

$$\begin{array}{lll} 4{\cdot}518 \times 10^{-8} & \text{cm.} \\ 5{\cdot}069 \quad ,, & ,, \\ 6{\cdot}737 \quad ,, & ,, \end{array}$$

Of these three crystals, the spacing of the first two would in any case not be observable in the present experiments, being so small that it would be just fully masked by experimental error. The observed spacing is definitely in best agreement with the long length of the cementite unit cell. We must therefore assume cementite present at the surface of the needle-tip, of the screw S (fig. 1), or of both. It must be further assumed that the cementite close to the surface was orientated so that the length of the orthorhombic unit cells was at right angles to the surface of the steel. This is in accord with what is found in the case of many crystals, and with what is found for thin layers of chain-compounds when forming a surface film on water.

The observed values of periodicity $(6{\cdot}4 \pm 0{\cdot}3) \,.\, 10^{-8}$ cm. and $(7{\cdot}0 \pm 0{\cdot}2) \,.\, 10^{-8}$ cm., both differ from the length of the cementite cell, $6{\cdot}737 \,.\, 10^{-8}$ cm., by slightly more than the probable errors, but fall on opposite sides of it in value.

We will now consider the evidence that the periodicities found are not spurious due to fortuitous circumstances; and also discuss theories as to the reason for the periodicity being observable in the optical lever experiments.

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* Heindlhofer, Phys. Rev. xxiv. pp. 426–438, Oct. 1924.

† Westgren and Phragmén, 'Nature,' cxiii. pp. 122–124, January 26th, 1924.

‡ Westgren and Phragmén, Journal Iron and Steel Inst. cix. pp. 159–172, 1924. (See also Internat. Crit. Tables, i. pp. 340, 349, and references.)

Evidence that the Periodicities found are not spurious.

Magnitude of the experimental errors.—It is best first to show that the accuracy of measurement was great enough to permit the detection of the periodicities.

The average accuracy of any single setting of the travelling microscope T (fig. 2) on the image F can be deduced (irrespective of any extra error due to a steady or gradually changing drift) by calculating in a number of cases the difference between any single setting and the mean of the ones immediately preceding and following it. The probable error value of these differences can be shown to be $\sqrt{3/2}$ times the probable error of a single setting.

Table IX.

Experiments.	Error of single microscope setting.	Error of single difference between consecutive microscope readings (each reading being the mean of ten settings).			
		Estimated by grouping the microscope settings in sets of five.		Deduced by comparison with best estimate of $n.\overline{D}$.	
		at microscope.	at lever.	at microscope.	at lever.
	$\times 10^{-4}$ cm.	$\times 10^{-4}$ cm.	$\times 10^{-8}$ cm.	$\times 10^{-4}$ cm.	$\times 10^{-8}$ cm.
Steel-mica	$\pm 2{\cdot}9$	$\pm 2{\cdot}8$	$\pm 1{\cdot}0$	$\pm 4{\cdot}1$	$\pm 1{\cdot}5$
	$\pm 3{\cdot}3$	$\pm 2{\cdot}8$	$\pm 1{\cdot}5$	$\pm 3{\cdot}4$	$\pm 1{\cdot}8$
Steel-steel	$\pm 1{\cdot}8$	$\pm 1{\cdot}5$	$\pm 0{\cdot}7$	$\pm 1{\cdot}8$	$\pm 0{\cdot}9$
	$\pm 2{\cdot}7$	$\pm 2{\cdot}0$	$\pm 1{\cdot}0$	$\pm 1{\cdot}9$	$\pm 1{\cdot}0$

The accuracy of the differences between successive microscope readings (each reading being the mean of ten settings) can be fairly estimated by comparing the results obtained by using only the first five settings in each group with the results obtained using only the last five settings in each group. This may somewhat underestimate any error due to a drift if it is present.

For comparison, the probable error value may be found of the deviation of any difference between successive microscope readings from the nearest integral multiple of the best estimate of the periodicity "unit length." (A set of these residuals was given in the last column of Table VII., and below was given the probable error value.)

These three estimates of error are summarized in Table IX., for the four sets of experiments.

It will be seen that the predicted errors (column 4) are on the whole slightly less than those apparently found (last column). Hence the personal errors of microscope setting, together with any small amount of general drift of readings, was not so large as to be likely to mask periodicities of the magnitude of those apparently detected. (The predicted errors are, as mentioned above, probably slightly underestimated.)

The small probability of obtaining spurious periodicities so well marked as those observed, and the small probability of such spurious periodicities so close to the expected values.—It will be convenient to consider the first set of measurements (Tables III. and VII.) to illustrate the method of calculation. Let us assume the points in fig. 3 to be distributed at random, instead of as observed. For any value of D chosen at random (except excessively large values) the chance of any one point falling within the limits $n \, . \, D \pm D/4$, where n is an integer, is 1/2. The chance (for any fixed value of D) of 18 or more out of 21 points falling within the above limits is

$$\frac{{}^{21}C_0+{}^{21}C_1+{}^{21}C_2+{}^{21}C_3}{2^{21}} = \frac{1}{1340} \text{ (approximately).}$$

(18 out of 21 observations fell between the above limits when $D=29{\cdot}4_5\times10^{-4}$ cm. at microscope—see fig. 3 and Table VIII.)

Now, when $D=\infty$, all the points fall within $\pm D/4$ of zero. As D is decreased steadily, a fresh arrangement of the 21 points in the compartments shown in fig. 3 occurs each time either boundary of any compartment passes any point. Each such transition is shown as a step in a graph such as fig. 4. Over any small range of the graph these transitions are independent, being due to different points (that were assumed distributed at random). Over a larger range the transitions are not strictly independent, but are sensibly so. Hence, usually about 1340 steps in the graph fig. 4 should contain (1 ± 1) peaks as high as 18 in 21 or higher. Now, the number of transitions between the observed peak and infinity is only 87 in the present instance. Hence, such a peak is not to be expected fortuitously anywhere between the observed position and infinity, its probability being only about 87/1340.

If we further assume the length of the mica unit cell as obtained by X-ray measurements * ($9{\cdot}95\times10^{-8}$ cm.), we can deduce the corresponding value of D in centimetres of microscope movement (limited by the probable errors of measurement of the optical lever length, and of the distance LF, fig. 2). The value so deduced in the present instance $(28{\cdot}0 \pm 1{\cdot}2) . 10^{-4}$ cm. at the microscope, falls 7 transitions away from the peak of the curve (fig. 4). The chance of obtaining a spurious peak of height (18 or more in 21) within 7 independent transitions of the expected place, when normally about 1340 such independent transitions would be required, is only 7/1340.

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* C. Mauguin, *loc. cit.*

Similar calculations have been made for the other three sets of observations, and are collected together (Table X.).

In the case of the steel-steel experiments the X-ray value of the length of the cementite unit cell has been used as the "expected value." No periodicity was expected when the experiments were made; but since only three spacings suggested by X-ray measurements are large enough to have been detectable, the order of magnitude of the probability will not be much changed.

Table X.

Experiment.	Height of peak in periodicity curve.	Number of random trials to obtain such a peak.	Actual number of trials between the peak and ∞.	Probability of such a peak fortuitously between the peak position and ∞.	Number of trials between the peak and the expected value.	Probability of such a peak fortuitously so near to the expected place.
Steel-mica	18 in 21	1340	87	0·065	7	0·005
	16 in 19	452	363	0·80	4	0·009
Steel-steel	16 in 18	1522	62	0·041	4	0·003
	18 in 21	1340	215	0·16	8†	0·006

† In this case the 8 are not independent, four being due to the largest reading (Table VI.). If this reading be omitted, however, the probability 0·006 is not measurably changed.

It will be seen that in three of the four cases such a peak would not have been expected as a result of fortuitous circumstances; and in all four cases its nearness to a value suggested by X-ray data cannot be attributed to chance.

Theories of the Action at the Contacts.

Three theories of the action at the contact have been considered. The detection of a periodicity might be attributed to a lateral movement of the mica (or the lever) during the tilting of the lever; or to an interpenetration of the crystal lattices of the two bodies between which contact is made; or to flow of one or both solids near the point of contact.

It was found that periodicity occurred even when the mica was fixed; and it occurred when the needle rested on the fixed steel below. By viewing the lever with a microscope it was found certainly not to move laterally by more than 0·005 mm. in the course of a dozen tiltings. To see what this implies it is necessary to estimate the area of contact at the needle-tip. The area of contact may be estimated by the calculations due to Hertz (though they are not strictly applicable to a sphere resting on a plane, nor unless both the bodies are isotropic). The radius of the circle of contact will be of the order

$$\sqrt[3]{\frac{3}{4}\left(\Sigma\frac{1-\sigma^2}{E}\right).r.P},$$

where r is the radius of curvature of the tip of the needle, σ and E are Poisson's ratio and Young's modulus for the materials, and P is the total static force. Since the mass of the lever was about 0·42 gram, and the centre of gravity was 0·5 mm. in front of the vertical plane through the outer legs (owing to a small projecting weight not shown in fig. 1), the static force at the contact is about 1700 dynes. Taking $r=0{\cdot}001$ cm. (see Table I.) and $\Sigma\frac{1-\sigma^2}{E}$ as about $2{\cdot}5\times10^{-12}$ cm.^{2}/dyne, we get the radius of the "circle" of contact to be of the order 0·0015 mm. Since a dozen tiltings did not produce any lateral movement as great as twice the estimated diameter of the circle of contact, it follows that lateral movement cannot be causing the thickness of the mica to be measured each time at an effectively different place; and hence such movement cannot account for the observed periodicity.

The second hypothesis (the interpenetration of the crystal lattices of the two bodies) would predict that the apparent change in thickness on tilting the lever, when it rested on mica, might be the sum or difference of integral multiples of the unit cell lengths of steel and mica. If this were so, the smaller steel periodicity would quite mask that due to the mica and prevent its detection. Hence this hypothesis also must be abandoned.

For the third hypothesis, that of flow of the solid near the point of contact, it is necessary to show that the pressure due to the lever may be large enough to produce movement.

Again following Hertz, the pressure at the centre of the circle of contact may be shown to be of the order

$$\frac{3}{2\pi}\left(\frac{4}{3r\Sigma\frac{1-\sigma^2}{E}}\right)^{2/3}\times P^{1/3}.$$

Hence, for the lever resting on mica, the pressure (if no flow took place) would reach the order 33,000 atmospheres. For the maximum possible free fall of the lever (0·0013 cm. at the needle-tip), the value might reach 80,000 atmospheres. And for steel on steel 180,000 atmospheres might be attained when such impact occurred. These estimated pressures appear to be as large as the likely values of the intrinsic pressures in mica and steel; and hence flow may be considered possible.

When steel rests on steel a flow of one or both is postulated. And when mica is interposed, it is assumed that the mica will flow and not the steel. This is likely, as it is well known that steel will easily scratch mica without being itself noticeably affected. The steel periodicity would thus not mask any due to the mica.

It is known that flow or slip takes place most readily parallel to a cleavage plane. And hence, when the needle impinges on the steel or mica we may postulate that a certain number of the surface layers of mica or steel are penetrated and then move fairly freely outwards parallel to the surface. The first layer not penetrated will then be bent by the needle reposing on it, and the area of contact must become so large that the pressure nowhere exceeds that required to cause penetration of the layer. The first layer not penetrated would thus settle the depth to which the needle descended; and, consequently, successive positions would differ by integral multiples of the unit cell length of the material below the needle (or of the material of the needle, if that were the more easily penetrated).

It is further necessary to explain why small *increases* in thickness are observed, that also show the unit cell periodicity. We may assume that when the needle is withdrawn, and the intense local pressure removed, surface tension or cohesion forces cause a return flow of the surface layers previously penetrated by the needle. This closing up (or partial closing) of a small pit in the surface may be compared with the aggregation of more or less isolated parts of thin metal films as found by Beilby[*]. In the case of the metal films the temperature had been raised somewhat, and the effect was probably not very rapid. However, in the present case the maximum increase found is only of the order of ten molecular or unit cells ; and on the removal of the intense local pressure this amount of return flow is not at all inconceivable.

In one respect the flow must differ from what Sir George Beilby considered took place on polishing a crystal surface[†]. It must here be assumed that the return flow takes place in layers that retain their thickness more or less unaltered, and do not become quite amorphous as Beilby supposed in his experiments.

Beilby, however, shows that subsequent crystallization of an isomorphous crystal on the polished surface took place with an orientation settled by the original crystal (unless the disturbed layer between were specially thick). And though he attributed this to action at a distance through the amorphous layer, it is conceivable that the layer is not perfectly amorphous. It might retain its layer formation approximately ; and in the present experiments the radial surface flow is probably more ordered than when polishing is performed by hand.

In conclusion, I should like to thank Prof. J. A. Crowther, in whose laboratory the work was carried out, for permitting and even encouraging what might be considered at least a speculative piece of research to undertake. To Prof. A. W. Porter my best thanks are due for his criticism and advice, which have contributed considerably to the completion of the work.

University of Reading,
Department of Physics,
December 31st, 1928.

[*] Proc. Roy. Soc. A, lxxii. pp. 232-3.

[†] *Op. cit.* lxxxii. p. 509.

CXXXII. *A Comparison of Whitehead's with Einstein's Law of Gravitation. By* WILLIAM BAND, *B.Sc., George Holt Physics Laboratory, The University of Liverpool* *.

1. *Foreword.*

IN a communication entitled "General Orbits in Relativity Dynamics by the Hamiltonian Method" (Phil. Mag. No. 284, pp. 277–292), G. Temple has shown that the dynamic invariants given by Einstein and Whitehead give precisely the same form to the equations of planetary orbits. His work, however, rests on the assumed distinctions between the metric and dynamic invariants ds and dJ respectively. If we follow Einstein and identify ds with dJ, then we find that Temple's Lagrange equations reduce to the identity $0=0$. In this case we must therefore examine Whitehead's invariant by the usual geodesic method, calculating the three-index symbols for the particular values of the fundamental tensor that he uses.

2. *Whitehead's First Expression.*

This can be written

$$ds^2=(1-2m/r)dt^2-(1+2m/r)dr^2$$
$$\pm 4m/r\,.\,dr\,dt-r^2d\theta^2-r^2\sin^2\theta d\phi^2$$
$$=g_{\mu\nu}\,dx_\mu\,dx_\nu,$$

where the indices refer to (r, θ, ϕ, t) taken in order, and where the unit of time is $3\,.\,10^{-10}$ second.

We then have

$$-g_{11}=1+2m/r$$
$$-g_{22}=r^2, \qquad -g_{33}=r^2\sin^2\theta$$
$$g_{14}=g_{41}=2m/r$$
$$g_{44}=1-2m/r$$

giving by the usual definition

$$-g^{11}=1-2m/r$$
$$-g^{22}=r^{-2}, \qquad -g^{33}=r^{-2}\sin^{-2}\theta$$
$$-g^{14}=-g^{41}=2m/r$$
$$g^{44}=1+2m/r.$$

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* Communicated by Prof. J. Rice, M.A.

Evaluating the three-index symbols defined by

$$[\mu\nu,\lambda]=\tfrac{1}{2}[\partial g_{\mu\lambda}/\partial x_\nu+\partial g_{\nu\lambda}/\partial x_\mu-\partial g_{\mu\nu}/\partial x_\lambda]$$

$$\{\mu\nu,\lambda\}=g^{\lambda\sigma}[\mu\nu,\sigma],$$

we find, when we neglect powers of r lower than -2,

$$\begin{array}{ll}
[11,1]=-m/r^2 & \{11,1\}=-m/r^2 \\
[11,4]=-2m/r^2 & \{11,4\}=-2m/r^2 \\
[22,1]=r & \{22,1\}=-r(1-2m/r) \\
 & \{22,4\}=-2m \\
[33,1]=r\sin\theta & \{33,1\}=-r\sin\theta(1-2m/r) \\
 & \{33,4\}=-2m\sin^2\theta \\
[33,2]=r^2\sin\theta\cos\theta & \{33,2\}=-\sin\theta\cos\theta \\
[44,1]=-m/r^2 & \{44,1\}=m/r^2 \\
 & \{44,4\}=\text{negligible}
\end{array}$$

$$\begin{array}{ll}
[21,2]=[12,2]=-r & \{21,2\}=\{12,2\}=1/r \\
[31,3]=[13,3]=-r\sin\theta & \{31,3\}=\{13,3\}=1/r \\
[41,4]=[14,4]=m/r^2 & \{41,4\}=\{14,4\}=m/r^2 \\
[23,3]=[32,3]=-r^2\sin\theta\cos\theta & \{23,3\}=\{32,3\}=\cot\theta
\end{array}$$

$$\{14,1\}=\{41,1\}=\text{negligible.}$$

We now obtain the geodesics defined by

$$d^2x_\alpha/ds^2+\{\mu\nu,\alpha\}dx_\mu/ds\,.\,dx_\nu/ds=0, \tag{1}$$

giving for the various values of α:—

1. $$d^2r/ds^2-mr^{-2}(dr/ds)^2-r(1-2m/r)(d\theta/ds)^2 \\ -r^2\sin^2\theta(1-2m/r)(d\phi/ds)^2+m/r^2(dt/ds)^2=0. \tag{2}$$

2. $$d^2\theta/ds^2+2/r\,.\,(dr/ds)(d\theta/ds)-\sin\theta\cos\theta(d\phi/ds)^2=0. \tag{3}$$

3. $$d^2\phi/ds^2+2/r\,.\,(dr/ds)(d\phi/ds) \\ +2\cot\theta(d\theta/ds)(d\phi/ds)=0. \tag{4}$$

4. $$d^2t/ds^2-mr^{-2}(dr/ds)^2-2m(d\theta/ds)^2 \\ -2m\sin^2\theta(d\phi/ds)^2+2m/r^2\,.\,(dr/ds)(dt/ds)=0. \tag{5}$$

If we arrange for θ to be zero, (3) shows that it remains zero, allowing us to write (4) and (5) in the simpler forms :

$$d^2\phi/ds^2+2/r\,.\,(dr/ds)(d\phi/ds)=0. \tag{4$'$}$$

$$d^2t/ds^2+2m/r^2(dr/ds)(dt/ds)=2m\{1-r^{-2}(dr/d\phi)^2\}(d\phi/ds)^2. \tag{5$'$}$$

Equation (4′) gives, as usual,

$$d\phi/ds=h/r^2. \tag{6}$$

Equation (6) shows that in (5′) the right-hand side may be equated approximately to zero, giving the usual solution

$$dt/ds = c(1+2m/r). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Putting θ zero in the expression for ds^2, we get

$$ds^2 = (1-2m/r)dt^2 - 4m/r \,.\, dr\,dt - (1+2m/r)dr^2 - r^2 d\phi^2. \quad (8)$$

Then by (6), (7), dividing through (8) by ds^2, we get

$$(1+2m/r)(dr/d\phi)^2(d\phi/ds)^2 = (1-2m/r)(dt/ds)^2$$
$$- r^2(d\phi/ds)^2 - 4m/r(dr/d\phi)(d\phi/ds)(dt/ds) - 1,$$

giving

$$(r^{-2}dr/d\phi)^2 = (1-4m/r)(1+4m/r)c^2/h^2$$
$$-(1-2m/r)/h^2 - (1-2m/r)/r^2$$
$$-4m/r(1-2m/r)(c^2/r^2)(1+2m/r)(1/h)dr/d\phi$$

or

$$\left[\frac{1}{r^2}dr/d\phi\right]^2 = (c^2-1)/h^2 + 2m/h^2 r$$
$$-1/r^2 + 2m/r^3 - (4mc/hr^2)dr/d\phi. \quad . \quad . \quad (9)$$

The equation corresponding to (9) arising from Einstein's expression for ds^2 is identical therewith, save for the term in $dr/d\phi$, which is there absent.

Now, if we are to neglect this term, we must confine our applications to motions in which the eccentricity of the orbit is small, for in other cases, *e.g.* motions of the comets, Whitehead's expression will no longer give correct results.

3. *Whitehead's Second Expression.*

Following Temple, we can write this:

$$ds^2 = (1-2m/r)dt^2 - 2\mathrm{F}(r)dr\,dt$$
$$-dr^2 - r^2 d\theta^2 - r^2\sin^2\theta d\phi^2, \quad . \quad . \quad (1)$$

where $\mathrm{F}(r)$ is a function of r only, tending to zero as r approaches infinity. We then have

$$-g_{11} = 1$$
$$-g_{22} = r^2, \qquad -g_{33} = r^2\sin^2\theta$$
$$-g_{14} = -g_{41} = \mathrm{F}(r)$$
$$g_{44} = 1 - 2m/r,$$

and since

$$-g^{11} = g_{44}[g_{14}{}^2 - g_{11}g_{44}]^{-1}$$
$$g^{14} = g^{41} = -g^{11}g_{14}/g_{44}$$
$$g^{44} = g^{11}g_{11}/g_{44},$$

we get, putting

$$\mathrm{R}\equiv[\mathrm{F}(r)^2+1-2m/r]\doteqdot 1, \quad . \quad . \quad . \qquad (2)$$

$$-g^{11}=(1-2m/r)\mathrm{R}^{-1}, \qquad g^{44}=1/\mathrm{R}$$

$$-g^{22}=r^{-2}, \qquad -g^{33}=r^{-2}\sin^{-2}\theta$$

$$-g^{14}=-g^{41}=\mathrm{F}(r)\mathrm{R}^{-1}.$$

From these the three-index symbols become

$\{11, 1\}=0$ $\qquad$ $\{44, 1\}=m(1--2m/r)/\mathrm{R}r^2$

$\{11, 4\}=-\mathrm{F}'(r)\,.\,\mathrm{R}^{-1}$ $\qquad$ $\{44, 4\}=m\mathrm{F}(r)/\mathrm{R}r^2$

$\{22, 1\}=-r(1-2m/r)\mathrm{R}^{-1}$ $\qquad$ $\{41, 4\}=\{14, 4\}=m/\mathrm{R}r^2$

$\{22, 4\}=-r\mathrm{F}(r)\mathrm{R}^{-1}$

$\{33, 1\}=-r\sin^2\theta(1-2m/r)\mathrm{R}^{-1}$ $\qquad$ $\{33, 4\}=-r\sin^2\theta\mathrm{F}'(r)\,.\,\mathrm{R}^{-1}$,

where the dash denotes differentiation with respect to r.

The rest remain as for the first expression (see § 2, above).

The geodesics for $\alpha=2, 3$ are precisely as before, giving, when θ is zero, the solution (6) of § 2.

The geodesic for α equals 4, then becomes, as a first approximation, the solution 2 (7).

The orbit is again obtained from the interval, giving

$$[1/r^2\,.\,dr/d\phi]^2=(c^2-1)/h^2-1/r^2+2mc^2/h^2r$$
$$-2\mathrm{F}\,.\,(c^2/h)(1+2m/r)(1/r^2\,.\,dr/d\phi). \quad . \qquad (3)$$

If in this we neglect the term in $dr/d\phi$, the orbit reduces to a Newtonian form.

Temple obtained the value

$$\mathrm{F}(r)=c\sqrt{2m/r}.$$

Putting this in (3), and remembering that for planetary motion h is of the order r, we see that even were we to retain the term in question, the correction involved therein is negligible in comparison with Einstein's correction to Newton. There appears to be no further significance to Temple's value for $\mathrm{F}(r)$.

4. *Conclusions.*

It appears that Whitehead's first $d\mathrm{J}^2$ is only approximate, and that his second is not even that, unless, as he assumes, the metric is independent of the gravitation field. Temple, however, having shown that the Einstein $d\mathrm{S}^2$ is satisfactory even on this last assumption, it has the double advantage of simplicity and independence of the particular theoretical interpretation.

CXXXIII. *The Motion of a Particle as a Statistical Problem and Bohr–Heisenberg's Uncertainty Conditions.* *By* D. MEKSYN *.

1. *Rigorous and Statistical Laws.*

THE laws of Physics are usually classified in two distinct groups: the rigorous laws of microscopic, and the statistical laws of macroscopic phenomena. The two classes of laws are quite different in their character. There can be no exception to rigorous laws; on the other hand, statistical laws give us only the probable course of a phenomenon. A body in a gravitational field must always move according to the same law; even a single exception would completely overturn the particular theory of gravitation adopted; on the other hand, statistical laws admit exceptions: heat may sometimes flow from a cold body to a hot one, this would not make the second law of Thermodynamics invalid.

The difference between these two classes of laws does not lie, however, in this particular point: we have practically just as little chance of observing heat flowing from a cold body to a hot one, as of seeing a body moving against the law of gravitation; the observed deviations from the second law are only confined to microscopic regions. What seems to be more important is the origin of these two categories of laws.

The rigorous laws of microscopic phenomena are considered to be laws of Nature; they do not depend upon the skill of the observer. Different is the origin of statistical laws; they are not prescribed laws of Nature, but are intimately connected with our nature and means of observation.

Two conditions are necessary in order that a statistical law may exist: (1) the particular system must be limited in such a way that every possible state of it shall have, although a small, yet a finite probability; (2) our means of observation must be such that we are able to measure only average values of quantities.

The development of Physics for the last twenty years, mainly in the theory of Radiation, has thrown some doubts on the validity of this classification.

As it is known, the line spectrum of a substance is due to jumping of electrons from one stable orbit into another; the intensity of such radiation is proportional to the number of atoms in which such changes take place, this number being governed by laws of probability. Hence the intensity of radiation is a purely statistical phenomenon. On the other hand, according to Bohr's Principle of Correspondence, the same intensity can be found, at least to the first approximation, from classical electrodynamics, based on rigorous laws of motion.

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* Communicated by the Author.

The case just mentioned may be a mere coincidence, which will be explained when we possess a rigorous theory of radiation, or perhaps the difficulty lies deeper in that the distinction between the laws is wrong.

2. *The Origin of Physical Laws.*

It may be that every microscopic phenomenon is governed by rigorous laws of Nature, and that a complex, or macroscopic phenomenon, is governed by statistical laws, which are substitute laws, which arise either because we do not yet know the microscopic law, or because our means of observation are too rough to follow each constituent separately (as in the theory of gases).

The other view is that microscopic laws do not exist, the behaviour of each constituent is possibly arbitrary (within certain limits), and is governed by laws of probability ; the observed laws of Nature are then influenced by the limitation of our means of observation.

If we meet a regularity in Nature it is because we observe either the average state of many systems, or of a single system during a relatively long interval of space and time.

We shall investigate the second point of view, and consider that the laws of Dynamics are only statistical laws.

DYNAMICS OF A MATERIAL POINT.

3. *Probability as the Basis of Laws of Motion.*

To find the laws of motion we must bear in mind the following consideration: in order that statistical laws may exist, every possible state must possess, if a small, yet a finite probability, and physical conditions must be regarded as imposing some limitations upon probabilities.

In the case of motion this means that the material point in a free space or in a field of force will be enclosed with great probability within a narrow cylindrical portion of the space, or in order that statistical laws of motion may exist there must be in space tracks of greatest probability.

We assume for the probability that an electron will describe some arbitrary track s' and not the track of greatest probability s (s' and s have the same ends) the well-known expression for the probability of errors

$$dW = Ce^{-\frac{(s'-s)^2}{\lambda^2}} d(s'-s). \quad . \quad . \quad . \quad . \quad (1)$$

If s is a geodesic line, the limits of $\Delta s = s' - s$ are 0 and ∞.

4. *The Law of Motion.*

From (1) it follows that the greatest probability will have the track for which

$$\Delta s = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At first sight (2) appears to be a mere repetition of the assumption that a track, s, exists which has the maximum probability.

But we may allow the equation (2) to define the track of greatest probability, and so suppose that we have to find s where

$$\Delta s = 0.$$

This equation is satisfied in so far as terms of the first order are concerned along a geodesic where

$$\delta s = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We come thus to the Law of Motion in the General Principle of Relativity.

Let us find the track, that will be observed. The coefficient C in (1) is found from

$$C \int_0^\infty e^{-\frac{x^2}{\lambda^2}} dx = 1$$

or
$$C = \frac{2}{\lambda \sqrt{\pi}},$$

and the average value of Δs in

$$\overline{\Delta s} = \frac{2}{\lambda \sqrt{\pi}} \int_0^\infty x e^{-\frac{x^2}{\lambda^2}} dx = \frac{\lambda}{\sqrt{\pi}}. \quad . \quad . \quad . \quad . \quad (4)$$

The equation (1) could also be interpreted as follows: the greatest probability is that for which ΔS is a small quantity; for a geodesic line the variations δx, δy, which make ΔS small, will have the greatest values. Or the particle has the greatest probability of motion in those parts, of space, where it can move with the greatest freedom.

We may say that the particle moves in geodesic regions. This permits of comparatively great variation of position and velocity. From equation (8), which follows later, it is easily seen that, for the hydrogen atom, these variations are of the same order of magnitude as the quantities themselves.

In order to complete the solution of our problem and obtain the actual form of the geodesic line, we must know the form of the phase space.

In two cases, at least, there is a definite solution, and this is for a uniform rectilinear motion, and for gravitation.

Several suggestions have been made as to the form of space in the case of the existence of an electromagnetic field. Kaluza, Klein, and others have suggested a five dimensional space, and in a recent paper * I have shown that, in the case of n electrons, a $4n$ dimensional space leads also to a geodesic motion.

5. *Limit of Exactness of Measurements.*

We have to fix λ. The dimension of $\frac{s}{c}$ is time, therefore $\frac{\lambda}{c}$ must be of the same dimension. We assume for $\frac{\lambda}{c}$ the period of de Broglie's wave associated with an electron or

$$\frac{\lambda}{c}=\frac{h}{mc^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This assumption, together with (4), leads us at once to Heisenberg's conditions for exactness of measurements.

From (4) and (5) we have

$$\overline{\Delta s} \sim \frac{h}{mc}. \quad . \quad . \qquad (5\,a)$$

For a geodesic line the first variation of s vanishes, and in order to find the meaning of (5 *a*) we have to evaluate the second variation of s. We could, however, also make use of the first variation, if only we carry out the integration not along a geodesic, but along a somewhat deformed line, whose first variation is equal to $\frac{\lambda}{\sqrt{\pi}}$.

We consider the case of a uniform rectilinear motion.

We have

$$\delta s=\delta\int_{t_1}^{t_2}(c^2\dot{t}^2-\dot{x}^2-\dot{y}^2-\dot{z}^2)^{\frac{1}{2}}\,dt$$

$$=\int_{t_1}^{t_2}\left\{\frac{d}{dt}\left(\frac{\dot{x}}{\sqrt{c^2-u^2}}\right).\delta x+\frac{d}{dt}\left(\frac{\dot{y}}{\sqrt{c^2-u^2}}\right).\delta y\right.$$

$$\left.+\frac{d}{dt}\left(\frac{\dot{z}}{\sqrt{c^2-u^2}}\right).\delta z-\frac{d}{dt}\left(\frac{c^2}{\sqrt{c^2-u^2}}\right).\delta t\right\}dt \quad (6)$$

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* Phil. Mag. 1928, p. 977.

or from (5a) and (6), since δx, δy, δz, δt are independent displacements, we obtain :

$$\left.\begin{array}{l}
\left|\overline{mc\int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{\dot{x}}{\sqrt{c^2-u^2}}\right)\delta x . dt}\right| \sim h, \\
\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\
\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\
\left|\overline{mc\int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{c^2}{\sqrt{c^2-u^2}}\right)\delta t . dt}\right| \sim h.
\end{array}\right\} \quad . \quad . \quad . \quad (7)$$

These equations could be also written, as (t_2-t_1) is small, as follows :—

$$\left.\begin{array}{l}
\overline{\delta p . \delta q} \sim h, \\
\cdot\quad\cdot\quad\cdot\quad\cdot \\
\cdot\quad\cdot\quad\cdot\quad\cdot \\
\overline{\delta \mathrm{E} . \delta t} \sim h,
\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where q, p, E denote the coordinates, momenta, and energy of an electron. These are Heisenberg's conditions.

The same equation (8) could also be obtained from the second varation from our geodesic line.

We have

$$\Delta \mathrm{S} = \frac{1}{\underline{|2}}\int_{t_1}^{t_2}\left(\frac{\partial^2 \mathrm{F}}{\partial \dot{x}^2}\,\delta\dot{x}^2 + 2\,\frac{\partial^2 \mathrm{F}}{\partial \dot{x}\,\partial \dot{y}}\,\delta\dot{x}\,\partial\dot{y} + \ldots\right)dt,$$

$$\sim \frac{h}{mc} \quad \text{on the average,}$$

where $\mathrm{F} = (c^2\dot{t}^2-\dot{x}^2-\dot{y}^2-\dot{z}^2)^{\frac{1}{2}}$.

For a velocity much less than c, we have

$$\frac{\partial^2 \mathrm{F}}{\partial \dot{x}^2} \overset{\frown}{=} \frac{1}{c},$$

hence

$$\int_{t_1}^{t_2}\delta\dot{x}^2\,dt \sim \frac{h}{m}$$

or

$$m(\delta\dot{x})^2\,\Delta t \sim h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now

$$\left.\begin{array}{l}
m\,\delta\dot{x} = \delta p, \\
\delta\dot{x}\,\Delta t = \delta(\dot{x}\,\Delta t) = \delta q,
\end{array}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

and from (9) and (10) we again obtain the first equation of (8).

In a recent paper Dr. H. T. Flint has suggested a different meaning for the conditions (1)*. It appears from some metrical considerations that the world line of an electron can be considered as made up of integral multiples of a fundamental length $s = \frac{h}{mc}$ (the velocity of light $t = 1$), and Dr. Flint has suggested that nothing less than this fundamental length could be directly or indirectly observed. The considerations developed in this paper provide a somewhat different explanation of this suggestion.

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* Roy. Soc. Proc. cxvii. p. 690.

In conclusion, we recapitulate the main ideas of this paper.

A particle does not possess a definite track, but moves in regions of greatest probability, hence all elements of motion are merely statistical quantities.

Laws of Physics can give us only the limitations upon probabilities. This is, for instance, the meaning of Schrödinger's Equation. This function provides us with a quantity for the measurement of the greatest probability of state. It does, however, not follow that an electron is forced to remain indefinitely in such a state. Given sufficient time it may deviate to such an extent from this position that it will come to another one of maximum probability. This is the cause of spontaneous radiation of an atom.

I wish to express my thanks to Dr. N. T. Flint for much useful criticism and assistance in the writing of this paper.

Added to the Proof.—We have assumed in (1) that the probability depends upon the length of a world track; this appears rather arbitrary. This assumption can, however, easily be connected with Schrödinger's Equation in relativistic form.

The approximate solution of this equation for a quasi-stationary motion is

$$\text{const.}\, e^{\frac{2\pi i}{h}\phi} \quad \phi = \int_{t_0}^{t} \rho_1 dx_1 + \rho_2 dx_2 + \rho_3 dx_3 - (\nu + \rho_4 c)dt,$$

where $\rho_1 \ldots \rho_4$ is the momentum energy vector, and ν is the potential of the external field.

Now ϕ can be transformed in

$$\phi = -\int_{t_0}^{t} \left(mc^2 \sqrt{1 - \frac{v^2}{c^2}} + \nu \right) dt,$$

which is the usual Hamiltonian, and (3) becomes $\delta\phi = 0$.

Wheatstone Laboratory,
King's College, London.
May 1st, 1929.

CXXXIV. *On Prof. R. D. Kleeman's Derivation of the Law of Mass Action.* *By* RICHARD F. GOLDSTEIN, *Ph.D.* *

IN the January number of the Philosophical Magazine † there appeared a letter by the present author, drawing attention to some errors invalidating the conclusions of an earlier paper of Prof. R. D. Kleeman ‡, in which he sought to disprove the classical Law of Mass Action.

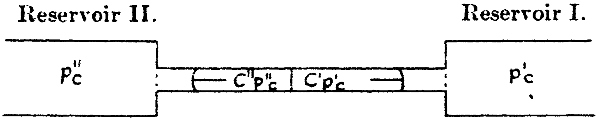
In reply §, Prof. Kleeman reiterated his original statements and invited the writer to develop his arguments further. He therefore takes this opportunity of doing so.

To follow Prof. Kleeman's nomenclature, in the reaction :—

$$aA + bB = cC + dD,$$

the molecules C, D are so-called "seprounstable," and on removal from the equilibrium box, dissociate spontaneously into their equilibrium mixtures. From this new standpoint, Prof. Kleeman developed his ideas.

For the sake of simplicity, consider first the species C.



c mols of C at pressure p''_c are removed from reservoir II. and immediately dissociate into their equilibrium mixture at pressure $C''\,p''_c$ still keeping the partial pressure of C at p''_c. According to Prof. Kleeman, the free energy change associated with this removal is nil. But since the dissociation of seprounstable molecules of C is a spontaneous process, it follows from the Second Law of Thermodynamics that the change must be associated with a diminution in free energy. Indeed, if the diminution in free energy in the spontaneous decomposition is zero, it necessarily follows that the change in free energy in the recombination of the decomposition mixture to pure C is also zero. To take a concrete example, if this were so, CO_2 at 900° C. would decompose into its equilibrium mixture of CO_2, CO and O_2 containing 25 per cent. CO_2 with no diminution in free energy, and we could recombine the gaseous mixture to CO_2 without the expenditure of any work.

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* Communicated by the Author.

† Phil. Mag. (7) vii. p. 205 (1929).

‡ *Ibid.* v. p. 263 (1928).

§ *Ibid.* vii. p. 206 (1929).

By removing the c mols of C from reservoir II. at pressure p''_C to a third reservoir, and then allowing C to decompose into its equilibrium mixture at pressure $C''p''_C$, the chief error in Prof. Kleeman's argument may be demonstrated even more clearly, since the spontaneous decomposition of C at pressure p''_C to give the gaseous equilibrium mixture at a higher pressure $C''p''_C$ may be made to do useful work, for example, by expansion against a constant pressure. The decomposition of the seprounstable molecules under isothermal reversible conditions must therefore be associated with a diminution in free energy, even allowing for the maintenance of the partial pressure of the seprounstable molecules at a constant value, and whether we obtain the decomposition products in two stages or in one.

On the return of the decomposition products of C at pressure $C'p'_C$ to reservoir I. as c mols of C at pressure p'_C, Prof. Kleeman has similarly and erroneously assumed that the recombination of the decomposition products to C takes place with no change in free energy. Since the decomposition and recombination of C take place at different pressures, the two equilibria are, in general, different and the two changes in free energy are not equivalent. Prof. Kleeman's main argument is therefore disproved.

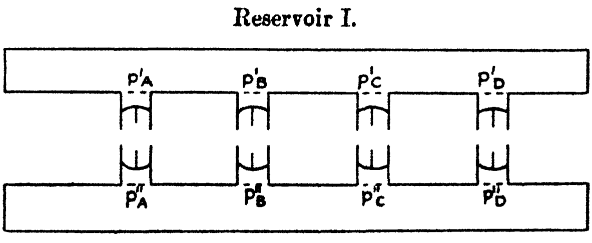
In like manner, the same arguments apply to the procedure adopted by Prof. Kleeman for the transference of d mols of D from reservoir II. at pressure p''_D to reservoir I. at pressure p'_D.

That van't Hoff's derivation of the Law of Mass Action is not invalidated by the concept of seprounstable molecules may be demonstrated by the following reasoning:—

In the change

$$aA+bB \rightleftharpoons cC+dD,$$

A, B being seprostable and C, D seprounstable



it is agreed that in the transference of a mols of A and b mols of B from reservoir I. to II. under isothermal, reversible conditions, the increase of free energy :

$$\Delta F_A + \Delta F_B = a\mathrm{RT}\ln\frac{p''_A}{p'_A} + b\mathrm{RT}\ln\frac{p''_B}{p'_B}.$$

For the transference of c mols of C and d mols of D from reservoir II. to I. under isothermal reversible conditions we have choice of several routes, along any of which the increase of free energy must be the same, since this depends solely on the initial and final states of the systems and not on the route chosen.

For example, we have among others the following options:—

(1) We can compress C and D from pressures p''_C, p''_D to p'_C, p'_D, without allowing any spontaneous decomposition to take place (for example, by carrying out the transference in infinitesimal time, or supposing the velocity of decomposition to be extremely small).

(2) We can remove C and D from reservoir II. at pressures p''_C, p''_D, allow them to decompose to the equilibrium mixtures at pressures $C''p''_C$, $D''p''_D$, recombine to C and D at pressures p''_C, p''_D, compress to pressures p'_e, p'_D and introduce into reservoir I.

(3) We can follow Prof. Kleeman's route, by removing C and D from reservoir II., allowing to decompose to mixtures at pressures $C''p''_C$, $D''p''_D$, compressing the mixtures to pressures $C'p'_C$, $D'p'_D$ (at which C and D have partial pressures p'_C, p'_D) recombining to C and D at pressures p'_C, p'_D, and introducing into reservoir I.

Whatever route we follow, the increment of free energy in the change of c mols of C and d mols of D from pressures p''_C p''_D to pressures p'_C, p'_D must be the same. And the increase in free energy in either routes (1) or (2) is obviously

$$\Delta F_C + \Delta F_D = c\mathrm{RT}\ln\frac{p'_C}{p''_C} + d\,\mathrm{RT}\ln\frac{p'_D}{p''_D}.$$

Since the net change in free energy in the whole process is zero,

$$\Delta F_A + \Delta F_B + \Delta F_C + F_D = 0$$

$$\text{or } a\,\mathrm{RT}\ln\frac{p''_A}{p'_A} + b\mathrm{RT}\ln\frac{p''_B}{p'_B} + c\mathrm{RT}\ln\frac{p'_C}{p''_C}$$

$$+ d\mathrm{RT}\ln\frac{p'_D}{p_D} = 0 \quad . \quad . \quad . \quad (1)$$

which leads by simple rearrangement to the classical van't Hoff equation.

It should be pointed out that the change in free energy in transfering the seprounstable molecules C and D from reservoir II. to reservoir I. by Prof. Kleeman's route cannot be calculated directly without assuming the Law of Mass Action, but recourse has to be had to alternative methods.

In his latest communication on this subject*, Prof. Kleeman endeavours to substantiate his conclusions by calculation of the work done instead of the free energy increments in the transference of the seprounstable molecules C and D from reservoir II. to I. by his route.

He states that equation (1) then assumes the form:

$$\mathrm{RT}\ln\frac{(p''_{\mathrm{C}})^c\,(p''_{\mathrm{D}})^d}{(p''_{\mathrm{A}})^a\,(p''_{\mathrm{B}})^b}+\mathrm{RT}\ln\frac{(p'_{\mathrm{C}})^c\,(p'_{\mathrm{D}})^d}{(p'_{\mathrm{A}})^a\,(p'_{\mathrm{B}})^b}+\mathrm{X}$$

where X is, in general, a finite quantity.

It should be sufficient to point out that if this is so, the the First Law of Thermodynamics is violated since a suitable cycle could be constructed which would produce useful work for an indefinite period.

Prof. Kleeman's kinetic derivation of his new law is equally fallacious.

In the equation

$$\mathrm{K}=\frac{\mathrm{K}_1k_1}{\mathrm{K}_2k_2},$$

k_1, k_2 express the chances of molecules encountering, and are a measure of the number of collisions taking place per unit time. Prof. Kleeman introduces two "activation" factors, K_1, K_2 which control the number of *effective* collisions that take place. That is to say, if in the reaction

$$2\mathrm{A}\rightleftharpoons 2\mathrm{B}$$

the number of collisions of a molecule A with another molecule A is k_1, the number of collisions leading to formation of B is K_1k_1, where K_1 is, in general, a number less than unity.

Now Prof. Kleeman goes on to say †, "But the quantities K_1, K_2, evidently depend on the frequencies of the encounters and on their nature, and are therefore functions of the fundamental independent variables, the volume of the mixture, its temperature, and the masses of the elemental constituents."

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* Phil. Mag. (7) vii. p. 206 (1929).

† *Ibid.* v. p. 271 (1928).

A more rigid proof than mere assertion would be welcome. The K's are ratios of effective collisions to total collisions, *i. e.*, derivatives of activity coefficients.

The writer must also take exception to Prof. Kleeman's equations (11) and (12) in his first paper*.

For the reaction:

$$2CO_2 \rightleftharpoons 2CO + O_2,$$

he writes:

$$K_1 k_1 C^2{}_{CO_2} = K_2 k_2 C^2{}_{CO} C_{O_2}, \quad . \quad . \quad . \quad . \quad (11)$$

whence he says

$$K = \frac{K_1 k_1}{K_2 k_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

but this implies that

$$K = \frac{C^2{}_{CO} C_{O_2}}{C^2{}_{CO_2}},$$

the equation he has been endeavouring to show is incorrect!

Finally, in his reply † to the writer, Prof. Kleeman in addition has been confusing activities with activity coefficients.

In the reaction, which he cites

$$2ce \rightleftharpoons c_2 + e_2,$$

the constant of mass action

$$K = \frac{(A_{ce})^2}{A_{c_2} A_{e_2}} = \frac{(\alpha_{ce} C_{ce})^2}{[\alpha_{c_2} C_{c_2}][\alpha_{e_2} C_{e_2}]}, \quad . \quad . \quad . \quad (2)$$

where the A's are *activities* and the α's *activity coefficients*.

From (2),

$$K = \frac{(\alpha^2{}_{ce})}{\alpha_{c_2} \alpha_{e_2}} \times \frac{C^2{}_{ce}}{C_{c_2} C_{e_2}},$$

which is of the same form as

$$K = \frac{K_1}{K_2} \times \frac{k_1}{k_2},$$

since k_1, k_2 represent the velocities of collision dependent on the concentration, and K_1, K_2, control the effectiveness of the collisions.

That is to say, K_1, K_2, are simple derivatives of the activity coefficients of the reagents.

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* Phil. Mag. (7) v. p. 271 (1928).

† *Ibid.* vii. p. 207 (1929).

CXXXV. *Notices respecting New Books.*

Revision of Rowland's Preliminary Table of Solar Spectrum Wave-lengths, with an Extension to the Recent Limit of the Infra-red. By Charles E. St. John, Charlotte E. Moore, Louise M. Ware, Edward F. Adams, and Harold D. Babcock. [Pp. xxi+238.] (Carnegie Institution of Washington: Publication No. 396. Papers of the Mount Wilson Observatory, Vol. III. 1928.)

THE publication of the revision of Rowland's solar wave-lengths has been eagerly awaited by spectroscopists. The investigations upon which it is based have been carried on at the Mount Wilson Observatory for more than a decade. The method of revision is summarized in the Introduction to the volume as follows:—

"The results rest upon two independent series of measurements; in each a large number of lines, well distributed and sufficiently isolated to serve for standards, have been measured. One series depends upon simultaneous exposures to the centre of the Sun and the standard iron arc with the 30-foot spectrograph and the 60-foot tower telescope in the earlier period, and with the 75-foot spectrograph and the 150-foot tower telescope in the later period. The other series was made with the interferometer, used at first with the spectrograph of the Snow telescope on Mount Wilson for the accessory dispersion, and later with the laboratory installation in Pasadena.

"The two series, corrected for the rotation and orbital motion of the earth, are in excellent agreement; the differences for individual lines rarely exceed 0·002 Å, while the systematic deviation is of the order of a few ten-thousandths of an angström. With the means of these two series as reference points, the wave-lengths of a still larger number of lines were interpolated upon spectrograms of high dispersion."

It is found that Rowland's wave-lengths are remarkably consistent for short spectral regions, but that over extended regions the corrections vary in a curiously progressive way.

The main table contains the wave-length of each line in the International System; the identification; the intensity; the intensities of lines in sun-spot spectra relative to the intensities in the spectrum of the disk; the temperature classification from furnace spectra; the classification from the behaviour of the lines under pressure, in the explosive spark and in the high-current arc; the excitation potential of all lines whose multiplet designations are known.

For completeness the Mount Wilson measures of the infra-red region from λ 7333 to λ 10218 are given in a separate table with additional information analogous to that given in the main table.

Separate lists are given of the strongest unidentified solar lines; of lines normally present in the chromosphere only; and of bright lines attributed to the corona. An additional table of great value contains the term designations for excitation potentials for the different atoms, including ionized atoms.

A list of 57 elements definitely identified in the Sun's atmosphere is given in the Introduction. Of the 35 elements not yet identified in the sun, 17 are regarded as possible and 18 as doubtfully possible of detection. Tables are given of the comparative representation of the elements and of the percentage of enhanced lines per element.

The volume reflects the highest credit upon the Mount Wilson Observatory and upon those who have collaborated in its production. It will prove of the greatest value to physicists and to astronomers.

The Collected Works of J. WILLARD GIBBS. Vol. I. *Thermodynamics.* [Pp. xxviii+434.] Vol. II. Part One. *Elementary Principles in Statistical Mechanics.* [Pp. xviii+207.] Part Two. *Dynamics*; *Vector Analysis and Multiple Algebra*; *Electromagnetic Theory of Light, &c.* [Pp. vi+284.] (New York and London: Longmans, Green and Co. 1928. Price 15*s.* each volume, or the two volumes 25*s.* net.)

THE former edition of Willard Gibbs's writings, published in 1906, has long been out of print. During the intervening years, there has been a greatly increased appreciation of the fundamental importance of his work, and, in particular, of his writings on the subjects of statistical mechanics and on the equilibrium of heterogeneous substances. The new reprint is therefore an event of importance, particularly as the volumes are offered at a price which should make them available to a wide circle of readers. This low published price has been made possible by the generosity of Professor Irving Fisher, of Yale University, a former pupil of Willard Gibbs, and by the employment of photographic methods of reproduction. The reproduction has been well done, and it is not easy to detect that the pages have not been printed from newly-set type.

The value of the present edition is increased by the inclusion of a reprint of Gibbs's treatise, "Elementary Principles in Statistical Mechanics." This was originally published as a separate book, and was not included in the former edition of the collected works. It has for some time been out of print. The present reprint is therefore the first complete edition of Gibbs's published writings.

The editors state that they have under consideration the publication, at a later date, of a commentary, written by recognized authorities in the several fields, designed to aid the student of Gibbs's writings. Such a volume would prove of undoubted value, and it is to be hoped that the project will be brought to fruition.

Modern Physics. By H. A. WILSON, M.A., D.Sc., F.R.S. [Pp. xiv+381.] (London: Blackie and Son. 1928. Price 30*s.* net.)

BASED on lectures given to students taking an Honours Course in physics, the volume contains a concise and up-to-date account of the present position of modern physics, suitable for advanced students. The subjects dealt with cover a wide range and are necessarily treated somewhat briefly. They include electron theory; theories of magnetism; thermionics; photoelectricity; quantum theory; the critical potentials of atoms; X-rays, cathode rays, α-, β-, and γ-rays; optical spectra; positive rays; radioactive transformations; constitution of atoms; gaseous ions; the motion of electrons in gases; the electrical conductivity of flames; the positive glow and negative glow; atmospheric electricity; special and general relativity and gravitation. At the end of each chapter, references are given to treatises on the subject-matter of the chapter, suitable for more advanced and specialized study.

A number of examples on the subject-matter of each chapter, to be worked by the student, are given at the end of the volume. In the mathematical sections, mathematical difficulties are carefully avoided; a chapter is devoted to vector operations in these dimensions, and the operations of tensor calculus are explained.

As an introduction to specialized study the volume can be thoroughly recommended.

The Conduction of Electricity through Gases. By Sir J. J. THOMSON, O.M., F.R.S., and G. P. THOMSON, M.A. Third Edition. Vol. I. [Pp. viii+491, with 121 figures.] (Cambridge: at the University Press. 1928. Price 25*s.* net.)

TWENTY-TWO years have elapsed since the publication of the second edition of Sir J. J. Thomson's well-known work on the conduction of electricity through gases. In the interval a vast number of researches on the subject have been published. The preparation of a new edition was commenced fifteen years ago, and the publication has at length become possible with the cooperation of Professor G. P. Thomson. Physicists will be grateful to the authors for having undertaken the very heavy task of summarizing the work that has been done since 1906.

It has been necessary to extend the book to two volumes. The volume under review covers the ground of the first ten chapters of the earlier edition, and deals with the general properties of the ions and with ionization by heat and light. Most of the original paragraphs have been retained with the original numbering; new paragraphs, dealing with subjects cognate to one of the original paragraphs, receive the same number, followed by a decimal. This procedure has the advantage of maintaining continuity with the earlier editions and of enabling the new material to be easily identified.

References to original papers are given throughout, and there are numerous diagrams of apparatus and experimental results. No physicist can afford to be without the authoritative account of an important branch of the subject.

The Nature of the Physical World. By A. S. EDDINGTON, M.A., LL.D., D.Sc., F.R.S. [Pp. ix+361.] (Cambridge: at the University Press. 1928. Price 12*s.* 6*d.* net.)

THE publication of the Gifford Lectures, delivered by Prof. Eddington in 1927, will make available to a wider circle a brilliant exposition of the nature of the physical world as viewed from the standpoint of modern science. The first portion of the book is devoted to the new scientific outlook. In Prof. Eddington's words: "The modern scientific theories have broken away from the common standpoint which identifies the real with the concrete." The new theories, which have brought about the downfall of classical physics,—relativity, the quantum theory, and wave-mechanics—are described; these chapters form a model of what popular scientific exposition should be—clear, accurate, and stimulating. The nature of the fundamental entities used in modern physics—length, mass, time, and so forth—is discussed at some length. The difference between the field laws of physics and the quantum laws is clearly elucidated: the former are shown to be mere truisms; the latter are regarded as laws of goverance of the material universe.

The latter portion of the book is more speculative, dealing with what the author terms "the problem of relating these purely physical discoveries to the wider aspects and interests of our human nature." The application of what Prof. Eddington terms the "principle of indeterminacy of behaviour" to the question of "free-will" provides interesting reading and has far-reaching consequences. The question as to whether our knowledge is confined to what we can discover by scientific methods has an application to the mind.

The volume is a masterly exposition which provides fascinating reading both for the scientist and for the philosopher.

Non-Riemannian Geometry. By L. P. EISENHART, Professor of Mathematics, Princeton University. American Mathematical Society Colloquim Publications, Vol. VIII. [Pp. viii+184.] (New York: 1928. English Agents, Bowes and Bowes, Cambridge. Price $2.50.)

THE recent developments of the theory of relativity have drawn attention to non-Riemannian geometry, and the appearance of this volume comes at an opportune time. The non-symmetric displacements which are at the basis of Einstein's latest theory are treated in the first chapter on asymmetric connexions, the projective geometry of paths, and the geometry of sub-spaces.

The volume is suitable for advanced mathematical students. Prof. Eisenhart's own contributions to the subject are considerable, and no better exposition of the mathematical theory could be desired. A full bibliography is appended and full references to it are given throughout the text. The volume forms an important addition to the valuable series of Colloquim Lectures published by the American Mathematical Society.

An Introduction to the Chemistry of Plant Products. Vol. I. *On the Nature and Significance of the Commoner Organic Components of Plants.* By P. HAAS, D.Sc., Ph.D., and T. G. HILL, D.Sc., A.R.C.S. Fourth Edition. [Pp. xvi+530.] (London: Longmans, Green and Co. 1928. Price 18*s.* net.)

THE fourth edition of Messrs. Haas and Hill's 'Chemistry of Plant Products' follows the same general lines as the third edition, when the work was divided into two volumes. The first volume deals mainly with the more chemical side of the subject—the occurrence and chemistry of the chief products of plant activity, such as fats, oils, waxes, aldehydes and alcohols, carbohydrates, glucosides, tannins, pigments, colloids, proteins, and enzymes. The more purely physiological problems are dealt with in the second volume.

The great increase in biochemical investigation during recent years has necessitated the inclusion of much additional matter, seven years having elapsed since the last edition appeared. The book has been thoroughly revised and to a large extent rewritten, and the volume under review contains 120 pages more than the previous edition.

The work is well annotated with references to original papers and has a detailed index. Both for study and reference the new edition will prove of great value to all engaged in biochemical work.

CXXXVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 904.]

March 6th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

Mrs. M. M. OGILVIE GORDON, D.Sc., F.G.S., delivered a lecture on the Structure of the Western Dolomites.

She described briefly the stratigraphical succession of the Permian and Triassic rocks which mainly compose the mountain-lands of the Western Dolomites, and showed their character in a number of photographic slides. Special attention was given to the outbreaks of volcanic action which took place in the Upper Buchenstein and Wengen periods at the close of the Alpine Middle Trias. These were associated with long crust-fissures in a west-north-westerly and east-south-easterly direction, in the course of which numerous vents occurred. Sills and dykes of andesite were much more frequent than had been supposed, although the sills were near the surface, and differed little from the lava-flows. Crust-movements took place, and certain areas were relatively uplifted as submarine terraces while inthrows occurred along the volcanic zones. Discordances and alternations were shown between the lavas and tuffs of the volcanic zones and the Marmolata Limestone or Schlern Dolomite that formed on the terraces.

Volcanic action continued in much lessened degree during the Cassian time, tuffs intermingling locally with the calcareous and marly deposits. The seas were shallower, and were marked out on the north of the tuff accumulations of Fassa into a number of protected basins. Growths of coral-limestone ('Cipit Limestone') were prevalent along the edges of the submarine terraces; they were frequently brecciated by surf action, and helped to extend the base upon which the limestone and dolomite of the terraces could form. Conditions, however, might vary, and the marly deposits and reef-limestones encroach upon the terrace-slopes.

Mojsisovic's presentation of the coral-reef origin of the great thicknesses of Schlern Dolomite was founded largely upon geological sections which showed the Wengen and Cassian strata banked up against steep walls of Schlern Dolomite, regarded as original reef-walls. But detailed observations over a wide area had shown a gradual passage of facies: for example, in Cassian time, from Cassian tuff-conglomerates, tuffs, and marls rich in fossils to lenticular reef-formations or blocks of Cipit Limestone, and from these to typical Schlern Dolomite. A number of photographs from the Fermeda group, Sella, Langkofl, and Schlern, demonstrated the passage of local alternations and facies. The facts pointed to algal formations as in great measure the origin of the Schlern Dolomite.

The next succeeding group of Raibl Sandstones and Marls also showed facies relations with the Schlern Dolomite. They had been deposited upon irregular surfaces of that dolomite, sometimes in shallow basin-shaped areas, sometimes on surfaces of abrasion. In the frequent unconformities, the upper layers of Raibl strata overstepped the lower. The group thus thinned, and passed into dolomitic facies in the direction in which the Schlern Dolomite swelled out in thickness.

An east-to-west section from the St. Cassian to the Ampezzo district showed the form of the Schlern Dolomite of that area, which in Lagazuoi Mountain was about 1600 feet thick, and thinned out gradually both towards east and west. Eastwards it thinned within 3 miles into the Cassian and Raibl strata of the Romerlo meadowland, westwards within 2½ miles into the same groups on the west of Valparola Alpe.

The **Dachstein Dolomite**, which succeeds the Raibl strata, forms a massive deposit throughout the Enneberg and Ampezzo district, but has been mostly eroded from the western area.

The leading structural features were described, with the aid of the geological map of the Gröden and Fassa district published by the lecturer in 1927. Several phases of mountain-movement could be distinguished in this district. During the regional movements of uplift of the Eastern Alps the whole district had been thrown into anticlines and synclines extending almost due east and west (N. 80°–85° W.). These were cut by numerous east-to-west vertical faults. Later, during periods of intensified crust-pressures, the faults were in many places overcast northwards or southwards, or in some oblique direction. The older fold-forms were locally thrown into steep knee-flexures, or new flexures developed, and new faults cut through them, usually with an inclination in one direction or another and the occurrence of local overthrusts.

Transverse vertical faults occurred at fairly regular intervals throughout the district, and at an advanced period, associated by the lecturer with the Dinaric (Peri-Adriatic) movements, cross-plication and cross-thrusting had been set up. The major fold-forms were of the nature of wide asymmetric anticlines with a steep western wing and a long gently-inclined eastern wing. The chief complications of the cross-movement occurred on the west side of these anticlines and in the areas of adjacent subsidence.

The vertical faults were in some cases overcast towards the west, or overcast folds formed and were fractured, and origin was given to the westward movement of thrust-masses.

Owing to recurrences of north-to-south pressures and to the marked inequalities of resistance, the later differential movements were extremely complex.

As a rule, gliding-planes developed within the thrust-masses themselves, and the upper layers tended to be carried farther forward than the lower.

A number of photographs of leading thrust-planes in the district and geological sections illustrated the relations of the thrust-masses of Pitschberg, on the north of Gröden Valley, Langkofl and Plattkofl, on the south of that Valley, and Buffaure, on the east of Fassa Valley. The horizontal displacements had not exceeded 2½ kilometres.

Reference was then briefly made to the next important zone of east-to-west thrust-movement, which the lecturer had demonstrated in 1899 in the Boe Summit of Sella Massive. Reithofer had recently shown an extension of this thrust in the north of the group, where he believed it to be a 'relief' overthrust. Dr. Ampferer was of opinion that quite a number of these later overthrusts were of this character.

Still farther east, the lecturer showed in her geological map of Enneberg the occurrence of another zone of east-to-west thrusts

on the east of the Lower Enneberg and St. Vigil area, a zone associated with overthrusts in the extensive tract of dolomite-rock between Enneberg and Ampezzo.

March 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communications were read:—

1. 'Some South Australian Algal Limestones in Process of Formation.' By Sir Douglas Mawson, O.B.E., B.E., D.Sc., F.R.S., F.G.S.

This contribution serves to record three different types of limestone now actually in process of formation, under the influence of plant-growth occurring in the south-eastern region of South Australia.

The locality is but slightly raised above sea-level and quite flat, but for a series of old vegetated calcareous sand-dunes which extend in parallel formation across the country, thus interfering with the drainage and determining low swampy intervening areas. It is an area of almost horizontal late Tertiary limestone.

A remarkable development of limestone-'biscuits' occurs at 'Biscuit Flat', a locality which is inundated in winter, but dries out in summer. The deposition of the calcium carbonate producing these forms is determined by the activities of blue-green algæ.

At a point near the coast, but isolated from the sea, are permanently inundated areas forming lakes of greater or less salinity. In Lake Karatta, one of these, an exuberant growth of algæ occurs, among which forms of *Lithothamnion* are conspicuous. Feeding upon the algæ are abundant shrimp-like crustaceans. A veritable reef of algal limestone is building out into the lake, comparable on a small scale with a fringing coral-reef.

Lakelets recently cut off from the Coorong, an arm of the sea, which usually dry up more or less completely during the summer months, are floored with a thick deposit of what is known locally as 'pipe-clay.' This proved to be a fine pulverulent deposit of calcium carbonate, somewhat dolomitized, evidently deposited from the saturated waters of the lakes during the spring season by the concentrating process of evaporation abetted by the presence of minute blue-green algæ.

2. 'The Unroofing of the Dartmoor Granite, and an Outline of the Distribution of its Detritus in the Sediments of Southern England.' By Arthur W. Groves, Ph.D., M.Sc., D.I.C.

A systematic outline mineralogical survey has been made of the sediments of Southern England, from the base of the Permian in Devon (Watcombe Clay) up to the Lenham Beds of the North Downs, in search of detrital minerals of the Dartmoor Granite. The work is based on the very detailed descriptions which have

been published by Dr. A. Brammall and others on the heavy mineral assemblages of the major granite-masses of Devon and Cornwall. Although it has been found possible to distinguish to a fair extent between the detritus from the various granites, the danger of confusing detrital material from Cornish granites with that from Dartmoor in the sediments of the South of England is largely obviated by the fact that detritus from the Cornish granites does not appear to have gone east of Dartmoor to any very appreciable extent, and that there are compartively few post-Carboniferous sedimentary strata west of Dartmoor.

For the sake of brevity, no reference is made in the paper to those horizons in which Dartmoor detritus was not found.

The minor intrusions above the granite were being rapidly eroded in Permo-Triassic times, but there is no evidence of the actual granite being exposed at that period. The minerals of the pneumatolytic and contact-zones of the minor intrusions consanguineous with the granite were distributed in large quantity east and north-east of the Dartmoor area, but no evidence of them was found in the Slapton outlier.

No proof has been obtained of direct derivation of detritus from the Dartmoor Granite in the Jurassic rocks.

The earliest evidence of the exposure of the granite is in late Wealden times. Aptian yields mostly negative evidence. Throughout Upper Cretaceous times—particularly during the Selbornian epoch—the Dartmoor Granite contributed enormous quantities of detritus to the sediments of Southern England, reaching as far afield as Kent and Oxfordshire, and perhaps farther.

The Thanet Sand is barren, and the Reading Beds yield but very scanty evidence. The London Clay appears to be barren, except in West Dorset. Dartmoor detritus is present again in large quantities in the Bagshot Beds of Devon and Dorset, but east of the New Forest the evidence of it is obscured by increasing quantities of material from Armorica. The higher Eocene strata have yielded negative evidence.

The Oligocene of the Isle of Wight also yielded negative evidence.

The Aquitanian deposits of the Bovey and Petrockstow basins are, as already shown by Prof. P. G. H. Boswell, mainly derived from the Dartmoor Granite.

The Cornish Pliocene was largely derived from the Cornish granites. The St. Keverne outlier is mainly derived from the Falmouth and Bodmin masses, and yields no evidence of Dartmoor detritus.

A number of new occurrences of dumortierite are recorded in the paper.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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